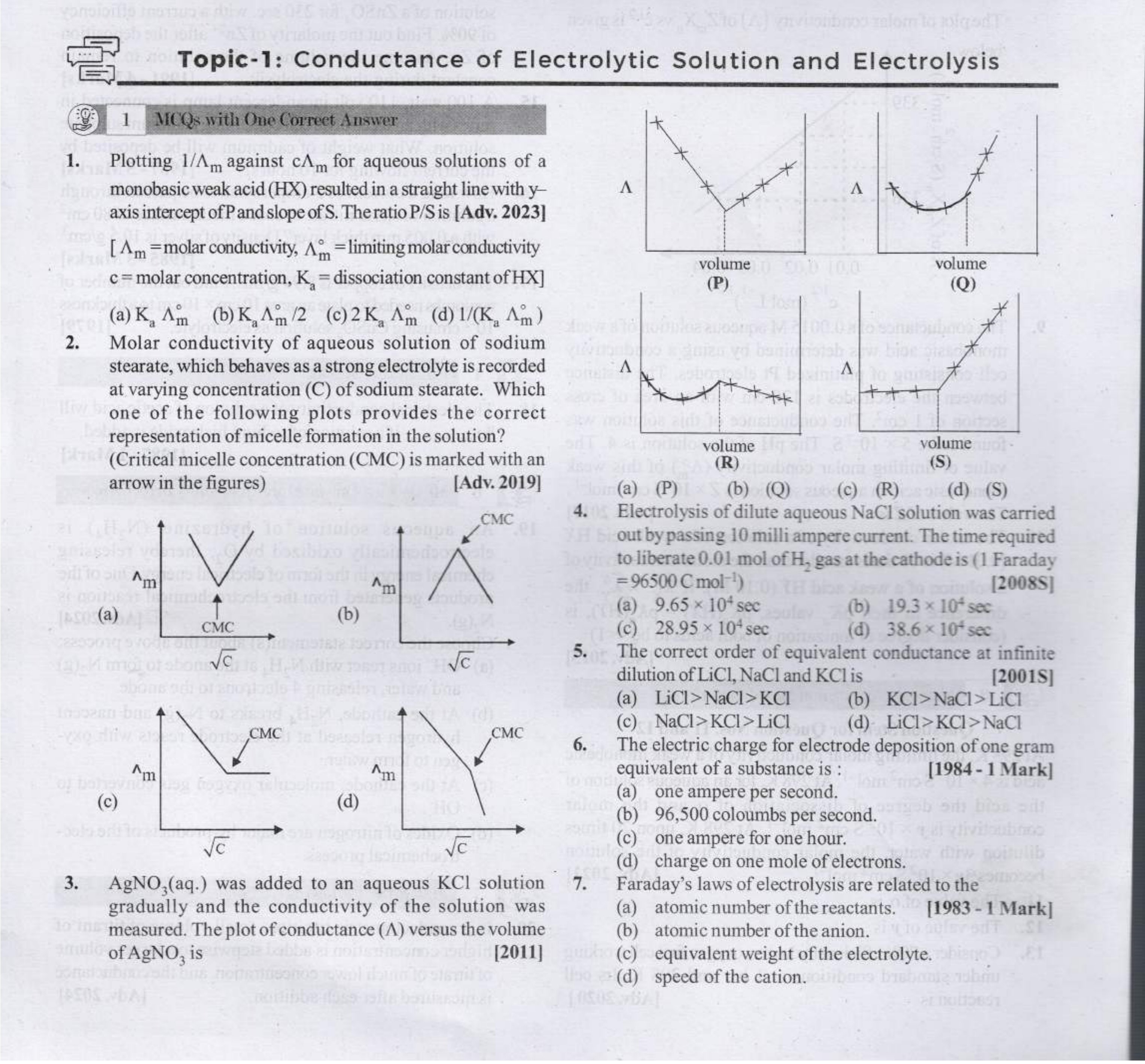
Chapter - Electrochemistry



Topic-1: Conductance of Electrolytic Solution and Electrolysis

1 MCQs with One Correct Answer

1. Plotting $1/\Lambda_m$ against $c\Lambda_m$ for aqueous solutions of a monobasic weak acid (HX) resulted in a straight line with y-axis intercept of P and slope of S. The ratio P/S is **[Adv. 2023]**

   [Λ_m = molar conductivity, Λ_m° = limiting molar conductivity

   c = molar concentration, K_a = dissociation constant of HX]

   (a) $K_a\Lambda_m^\circ$ (b) $K_a\Lambda_m^\circ/2$ (c) $2K_a\Lambda_m^\circ$ (d) $1/(K_a\Lambda_m^\circ)$

2. Molar conductivity of aqueous solution of sodium stearate, which behaves as a strong electrolyte is recorded at varying concentration (C) of sodium stearate. Which one of the following plots provides the correct representation of micelle formation in the solution? (Critical micelle concentration (CMC) is marked with an arrow in the figures) **[Adv. 2019]**

3. $AgNO_3$(aq.) was added to an aqueous KCl solution gradually and the conductivity of the solution was measured. The plot of conductance (Λ) versus the volume of $AgNO_3$ is **[2011]**

   (a) (P) (b) (Q) (c) (R) (d) (S)

4. Electrolysis of dilute aqueous NaCl solution was carried out by passing 10 milli ampere current. The time required to liberate 0.01 mol of H_2 gas at the cathode is (1 Faraday = 96500 C mol^{-1}) **[2008S]**

   (a) 9.65×10^4 sec (b) 19.3×10^4 sec
   (c) 28.95×10^4 sec (d) 38.6×10^4 sec

5. The correct order of equivalent conductance at infinite dilution of LiCl, NaCl and KCl is **[2001S]**

   (a) LiCl > NaCl > KCl (b) KCl > NaCl > LiCl
   (c) NaCl > KCl > LiCl (d) LiCl > KCl > NaCl

6. The electric charge for electrode deposition of one gram equivalent of a substance is : **[1984 - 1 Mark]**

   (a) one ampere per second.
   (b) 96,500 coloumbs per second.
   (c) one ampere for one hour.
   (d) charge on one mole of electrons.

7. Faraday's laws of electrolysis are related to the

   (a) atomic number of the reactants. **[1983 - 1 Mark]**
   (b) atomic number of the anion.
   (c) equivalent weight of the electrolyte.
   (d) speed of the cation.

2 Integer Value Answer

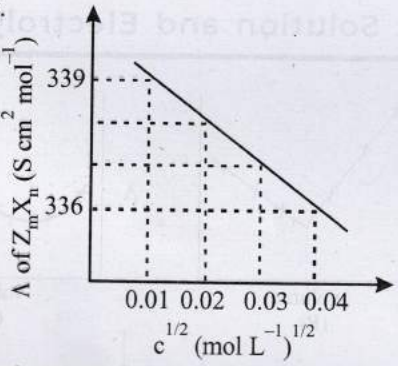
8. Consider the strong electrolytes Z_mX_n, U_mY_p and V_mX_n. Limiting molar conductivity (Λ^0) of U_mY_p and V_mX_n are 250 and 440 S cm^2 mol^{-1}, respectively. The value of $(m+n+p)$ is ______. **[Adv. 2022]**

Given:

Ion	Z^{n+}	U^{p+}	V^{n+}	X^{m-}	Y^{m-}
$\lambda^0\left(\text{S cm}^2\ \text{mol}^{-1}\right)$	50.0	25.0	100.0	80.0	100.0

λ^0 is the limiting molar conductivity of ions.

The plot of molar conductivity (Λ) of Z_mX_n vs $c^{1/2}$ is given below.



9. The conductance of a 0.0015 M aqueous solution of a weak monobasic acid was determined by using a conductivity cell consisting of platinized Pt electrodes. The distance between the electrodes is 120 cm with an area of cross section of 1 cm^2. The conductance of this solution was found to be 5×10^{-7} S. The pH of the solution is 4. The value of limiting molar conductivity (Λ_m°) of this weak monobasic acid in aqueous solution is $Z \times 10^2$ S cm^2 mol^{-1}. The value of Z is **[Adv. 2017]**

10. The molar conductivity of a solution of a weak acid HX (0.01 M) is 10 times smaller than the molar conductivity of a solution of a weak acid HY (0.10 M). If $\lambda^0_{X^-} \approx \lambda^0_{Y^-}$ the difference in their pK_a values, $pK_a(HX) - pK_a(HY)$, is (consider degree of ionization of both acids to be <<1) **[Adv. 2015]**

3 Numeric / New Stem Based Questions

Question Stem for Question Nos. 11 and 12

At 298 K, the limiting molar conductivity of a weak monobasic acid is 4×10^2 S cm^2 mol^{-1}. At 298 K, for an aqueous solution of the acid the degree of dissociation of α and the molar conductivity is $y \times 10^2$ S cm^2 mol^{-1}. At 298 K, upon 20 times dilution with water, the molar conductivity of the solution becomes $3y \times 10^2$ S cm^2 mol^{-1}. **[Adv. 2021]**

11. The value of α is ____.

12. The value of y is ____.

13. Consider a 70% efficient hydrogen-oxygen fuel cell working under standard conditions at 1 bar and 298 K. Its cell reaction is **[Adv. 2020]**

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l).$$

The work derived from the cell on the consumption of 1.0×10^{-3} mol of $H_2(g)$ is used to compress 1.00 mol of a monoatomic ideal gas in a thermally insulated container. What is the change in the temperature (in K) of the ideal gas?

The standard reduction potentials for the two half-cells are given below.

$$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l),\ E^0 = 1.23\,V,$$

$$2H^+(aq) + 2e^- \rightarrow H_2(g),\ E^0 = 0.00\,V$$

Use $F = 96500$ C mol^{-1}, $R = 8.314$ J mol^{-1} K^{-1}.

14. A current of 1.70 A is passed through 300.0 mL of 0.160 M solution of a $ZnSO_4$ for 230 sec. with a current efficiency of 90%. Find out the molarity of Zn^{2+} after the deposition of Zn. Assume the volume of the solution to remain constant during the electrolysis. **[1991 - 4 Marks]**

15. A 100 watt, 110 volt incandescent lamp is connected in series with an electrolyte cell containing cadmium sulphate solution. What weight of cadmium will be deposited by the current flowing for 10 hours? **[1987 - 5 Marks]**

16. How long a current of 3 ampere has to be passed through a solution of silver nitrate to coat a metal surface of 80 cm^2 with a 0.005 mm thick layer? Density of silver is 10.5 g/cm^3. **[1985 - 3 Marks]**

17. The density of copper is 8.94 g/mL. Find out the number of coulombs needed to plate an area 10 cm × 10 cm to a thickness 10^{-2} cm using $CuSO_4$ solution as electrolyte. **[1979]**

4 Fill in the Blanks

18. The electrical conductivity of a solution of acetic acid will be .... if a solution of sodium hydroxide is added. **[1987 - 1 Mark]**

6 MCQs with One or More than One Correct Answer

19. An aqueous solution of hydrazine (N_2H_4) is electrochemically oxidized by O_2, thereby releasing chemical energy in the form of electrical energy. One of the products generated from the electrochemical reaction is $N_2(g)$. **[Adv. 2024]**

Choose the correct statement(s) about the above process:

(a) OH^- ions react with N_2H_4 at the anode to form $N_2(g)$ and water, releasing 4 electrons to the anode.

(b) At the cathode, N_2H_4 breaks to $N_2(g)$ and nascent hydrogen released at the electrode reacts with oxygen to form water.

(c) At the cathode, molecular oxygen gets converted to OH^-.

(d) Oxides of nitrogen are major by-products of the electrochemical process.

7 Match the Following

20. In a conductometric titration, small volume of titrant of higher concentration is added stepwise to a larger volume of titrate of much lower concentration, and the conductance is measured after each addition. **[Adv. 2024]**

The limiting ionic conductivity (Λ_0) values (in mS m^2 mol^{-1}) for different ions in aqueous solutions are given below:

Ions	Ag^+	K^+	Na^+	H^+	NO_3^-	Cl^-	SO_4^{2-}	OH^-	CH_3COO^-
Λ_0	6.2	7.4	5.0	35.0	7.2	7.6	16.0	19.9	4.1

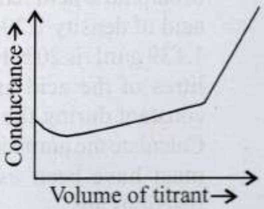
For different combinations of titrates and titrants given in **List-I**, the graphs of 'conductance' versus 'volume of titrant' are given in **List-II**.

Match each entry in **List-I** with the appropriate entry in **List-II** and choose the correct option.

List-I **List-II**

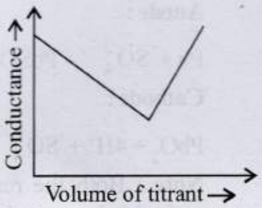
(P) Titrate: KCl
Titrant: $AgNO_3$

(1)



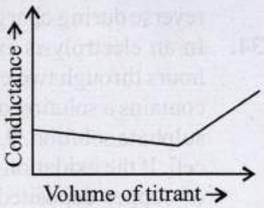
(Q) Titrate: $AgNO_3$
Titrant: KCl

(2)



(R) Titrate: NaOH
Titrant: HCl

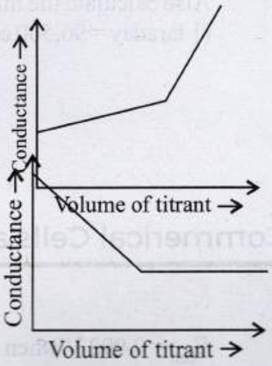
(3)



(S) Titrate: NaOH
Titrant: CH_3COOH

(4)

(5)



(a) P-4, Q-3, R-2, S-5 (b) P-2, Q-4; R-3; S-1
(c) P-3, Q-4, R-2, S-5 (d) P-4; Q-3; R-2; S-1

21. An aqueous solution of X is added slowly to an aqueous solution of Y as shown in List I. The variation in conductivity of these reactions is given in List II. Match list I with List II and select the correct answer using the code given below the lists : **[Adv. 2013]**

	List-I		List-II
P.	$\underset{X}{(C_2H_5)_3N} + \underset{Y}{CH_3COOH}$	1.	Conductivity decreases and then increases
Q.	$\underset{X}{KI(0.1M)} + \underset{Y}{AgNO_3(0.01M)}$	2.	Conductivity decreases and then does not change much
R.	$\underset{X}{CH_3COOH} + \underset{Y}{KOH}$	3.	Conductivity increases and then does not change much
S.	$NaOH + HI$ X Y	4.	Conductivity does not change much and then increases

Codes :

	P	Q	R	S
(a)	3	4	2	1
(b)	4	3	2	1
(c)	2	3	4	1
(d)	1	4	3	2

22. Match the following, choosing one item from column **X** and one from column **Y**. **[Multiple Concepts, 1982 - 2 Marks]**

	X		Y
(i)	neutrons	(p)	Kohlrausch
(ii)	molecular speed	(q)	van der Waals
(iii)	intermolecular forces	(r)	Maxwell
(iv)	conductance of ions	(s)	Chadwick

8 Comprehension/Passage Based Questions

Chemical reactions involve interaction of atoms and molecules. A large number of atoms/molecules (approximately 6.023×10^{23}) are present in a few grams of any chemical compound varying with their atomic/molecular masses. To handle such large numbers conveniently, the mole concept was introduced. This concept has implications in diverse areas such as analytical chemistry, biochemistry, electrochemistry and radiochemistry. The following example illustrates a typical case, involving chemical/electrochemical reaction, which requires a clear understanding of the mole concept.

A 4.0 molar aqueous solution of NaCl is prepared and 500 mL of this solution is electrolysed. This leads to the evolution of chlorine gas at one of the electrodes (atomic mass : Na = 23, Hg = 200; 1 Faraday = 96500 coulombs).

23. The total number of moles of chlorine gas evolved is **[2007]**
(a) 0.5 (b) 1.0 (c) 2.0 (d) 3.0

24. If the cathode is a Hg electrode, the maximum weight (g) of amalgam formed from this solution is **[2007]**
(a) 200 (b) 225 (c) 400 (d) 446

25. The total charge (coulombs) required for complete electrolysis is **[2007]**
(a) 24125 (b) 48250 (c) 96500 (d) 193000

10 Subjective Problems

26. We have taken a saturated solution of AgBr. K_{sp} of AgBr is 12×10^{-14}. If 10^{-7} mole of $AgNO_3$ are added to 1 litre of this solution, find conductivity (specific conductance) of this solution in terms of 10^{-7} S m^{-1} units. Given, Molar conductance of Ag^+, Br^- and NO_3^- are 6×10^{-3} Sm^{2}mol^{-1}, 8×10^{-3} Sm^{2}mol^{-1} and 7×10^{-3} Sm^{2}mol^{-1}. **[2006 - 6M]**

27. Copper sulphate solution (250 mL) was electrolysed using a platinum anode and a copper cathode. A constant current of 2 mA was passed for 16 minutes. It was found that after electrolysis, the absorbance of the solution was reduced to 50% of its original value. Calculate the concentration of copper sulphate in the solution to begin with. **[2000 - 3 Marks]**

28. How many grams of silver could be plated out on a serving tray by electrolysis of a solution containing silver in +1 oxidation state for a period of 8.0 hours at a current of 8.46 amperes? What is the area of the tray if the thickness of the silver plating is 0.00254 cm? Density of silver is 10.5 g/cm^3. **[1997 - 3 Marks]**

29. Chromium metal can be plated out from an acidic solution containing CrO_3 according to the following equation.

$$CrO_3(aq) + 6H^+(aq) + 6e^- \rightarrow Cr(s) + 3H_2O$$

Calculate (i) how many grams of chromium will be plated out by 24,000 coulombs and (ii) how long will it take to plate out 1.5 g of chromium by using 12.5 amp current. **[1993 - 2 Marks]**

30. Calculate the quantity of electricity that would be required to reduce 12.3 g of nitrobenzene to aniline, if the current efficiency for the process is 50 per cent. If the potential drop across the cell is 3.0 volts, how much energy will be consumed? **[1990 - 3 Marks]**

31. An acidic solution of Cu^{2+} salt containing 0.4 g of Cu^{2+} is electrolysed until all the copper is deposited. The electrolysis is continued for seven more minutes with the volume of solution kept at 100 mL. and the current at 1.2 amp. Calculate the volume of gases evolved at NTP during the entire electrolysis. **[1989 - 5 Marks]**

32. In a fuel cell, hydrogen and oxygen react to produce electricity. In the process, hydrogen gas is oxidised at the anode and oxygen at the cathode. If 67.2 litre of H_2 at STP react in 15 minutes, what is the average current produced? If the entire current is used for electro deposition of copper from copper (II) solution, how many grams of copper will be deposited? **[1988 - 4 Marks]**

Anode reaction : $H_2 + 2OH^- \rightarrow 2H_2O + 2e^-$

Cathode reaction : $\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^-$.

33. During the discharge of a lead storage battery, the density of sulphuric acid fell from 1.294 to 1.139 g/mL. Sulphuric acid of density 1.294 g/mL is 39% by weight and that of 1.139 g/mL is 20% H_2SO_4 by weight. The battery holds 3.5 litres of the acid and the volume remained practically constant during the discharge.

Calculate the number of ampere-hours for which the battery must have been used. The charging and discharging reactions are : **[1986 - 5 Marks]**

Anode :

$Pb + SO_4^{2-} = PbSO_4 + 2e^-$ (discharging)

Cathode :

$PbO_2 + 4H^+ + SO_4^{2-} + 2e^- = PbSO_4 + 2H_2O$ (discharging)

Note : Both the reactions take place at the anode and cathode respectively during discharge. Both reaction get reverse during charging.

34. In an electrolysis experiment, current, was passed for 5 hours through two cells connected in series. The first cell contains a solution of gold and the second contains copper sulphate solution. 9.85 g of gold was deposited in the first cell. If the oxidation number of gold is +3, find the amount of copper deposited on the cathode of the second cell. Also calculate the magnitude of the current in amperes. (1 faraday = 96,500 coulombs) **[1983 - 3 Marks]**

Topic-2: Nernst Equation, Commerical Cells and Corrosion

1 MCQs with One Correct Answer

1. For the following cell,

$Zn(s) \mid ZnSO_4(aq) \parallel CuSO_4(aq) \mid Cu(s)$

when the concentration of Zn^{2+} is 10 times the concentration of Cu^{2+}, the expression for ΔG (in J mol^{-1}) is [F is Faraday constant; R is gas constant; T is temperature; E^0 (cell) = 1.1 V] **[Adv. 2017]**

(a) $1.1F$ (b) $2.303RT - 2.2F$

(c) $2.303RT + 1.1F$ (d) $-2.2F$

2. For the following electrochemical cell at 298 K,

$Pt(s) \mid H_2(g, 1\ bar) \mid H^+(aq, 1\ M) \parallel M^{4+}(aq), M^{2+}(aq) \mid Pt(s)$

$E_{cell} = 0.092$ V when $\dfrac{[M^{2+}(aq)]}{[M^{4+}(aq)]} = 10^x$. **[Adv. 2016]**

Given : $E^\circ_{M^{4+}/M^{2+}} = 0.151$ V; $2.303\dfrac{RT}{F} = 0.059$ V.

The value of x is

(a) –2 (b) –1 (c) 1 (d) 2

3. Consider the following cell reaction: **[2011]**

$2Fe(s) + O_2(g) + 4H^+(aq) \rightarrow 2Fe^{2+}(aq) + 2H_2O(l); E^\circ = 1.67V$

At $[Fe^{2+}] = 10^{-3}$ M, $P(O_2) = 0.1$ atm and pH = 3, the cell potential at 25°C is

(a) 1.47V (b) 1.77V (c) 1.87V (d) 1.57V

4. The rusting of iron takes place as follows **[2005S]**
$2H^+ + 2e^- + \frac{1}{2}O_2 \longrightarrow H_2O(l)\,;\, E° = +1.23$ V
$Fe^{2+} + 2e^- \longrightarrow Fe(s)\,;\, E° = -0.44$ V
Calculate $\Delta G°$ for the net process
(a) -322 kJ mol^{-1} (b) -161 kJ mol^{-1}
(c) -152 kJ mol^{-1} (d) -76 kJ mol^{-1}

5. The emf of the cell **[2004S]**
$Zn\,|\,Zn^{2+}\,(0.01\ M)\,||\,Fe^{2+}\,(0.001\ M)\,|\,Fe$
at 298 K is 0.2905 then the value of equilibrium constant for the cell reaction is
(a) $e^{\frac{0.32}{0.0295}}$ (b) $10^{\frac{0.32}{0.0295}}$ (c) $10^{\frac{0.26}{0.0295}}$ (d) $10^{\frac{0.32}{0.0591}}$

6. In the electrolytic cell, flow of electrons is from **[2003S]**
(a) Cathode to anode in solution
(b) Cathode to anode through external supply
(c) Cathode to anode through internal supply
(d) Anode to cathode through internal supply

7. Standard electrode potential data are useful for understanding the suitability of an oxidant in a redox titration. Some half cell reactions and their standard potentials are given below : **[2002S]**

$$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l) \qquad E° = 1.51\ V$$

$$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l) \qquad E° = 1.38\ V$$

$$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq) \qquad E° = 0.77\ V$$

$$Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq) \qquad E° = 1.40\ V$$

Identify the only incorrect statement regarding the quantitative estimation of aqueous $Fe(NO_3)_2$
(a) MnO_4^- can be used in aqueous HCl
(b) $Cr_2O_7^{2-}$ can be used in aqueous HCl
(c) MnO_4^- can be used in aqueous H_2SO_4
(d) $Cr_2O_7^{2-}$ can be used in aqueous H_2SO_4

8. Saturated solution of KNO_3 is used to make 'salt–bridge' because **[2001S]**
(a) velocity of K^+ is greater than that of NO_3^-
(b) velocity of NO_3^- is greater than that of K^+
(c) velocities of both K^+ and NO_3^- are nearly the same
(d) KNO_3 is highly soluble in water

9. For the electrochemical cell, $M\,|\,M^+\,||\,X^-\,|\,X, E°(M^+/M) = 0.44$V and $E°(X/X^-) = 0.33$V.
From this data one can deduce that **[2000S]**
(a) $M + X \rightarrow M^+ + X^-$ is the spontaneous reaction
(b) $M^+ + X^- \rightarrow M + X$ is the spontaneous reaction
(c) $E_{cell} = 0.77$V
(d) $E_{cell} = -0.77$V

10. A gas *X* at 1 atm is bubbled through a solution containing a mixture of 1 M Y^- and 1 M Z^- at 25°C. If the reduction potential of $Z > Y > X$, then, **[1999 - 2 Marks]**
(a) *Y* will oxidize *X* and not *Z*
(b) *Y* will oxidize *Z* and not *X*
(c) *Y* will oxidize both *X* and *Z*
(d) *Y* will reduce both *X* and *Z*

11. The standard reduction potentials of $Cu^{2+}\,|\,Cu$ and $Cu^{2+}\,|\,Cu^+$ are 0.337 V and 0.153 respectively. The standard electrode potential of $Cu^+\,|\,Cu$ half cell is **[1997 - 1 Mark]**
(a) 0.184V (b) 0.827V (c) 0.521V (d) 0.490V

12. A dilute aqueous solution of Na_2SO_4 is electrolyzed using platinum electrodes. The products at the anode and cathode are: **[1996 - 1 Mark]**
(a) O_2, H_2 (b) $S_2O_8^{2-}$, Na
(c) O_2, Na (d) $S_2O_8^{2-}, H_2$

13. The standard oxidation potentials, $E°$, for the half reactions are as **[1988 - 1 Mark]**
$Zn = Zn^{2+} + 2e^-\,;\, E° = +0.76$ V
$Fe = Fe^{2+} + 2e^-\,;\, E° = +0.41$ V
The EMF for the cell reaction :
$Fe^{2+} + Zn \rightarrow Zn^{2+} + Fe$
(a) -0.35 V (b) $+0.35$ V (c) $+1.17$ V (d) -1.17 V

14. A solution of sodium sulphate in water is electrolysed using inert electrodes. The products at the cathode and anode are respectively **[1987 - 1 Mark]**
(a) H_2, O_2 (b) O_2, H_2 (c) O_2, Na (d) O_2, SO_2

15. The reaction : **[1985 - 1 Mark]**
$\frac{1}{2}H_2(g) + AgCl(s) \rightarrow H^+(aq) + Cl^-(aq) + Ag(s)$
occurs in the galvanic cell
(a) $Ag\,|\,AgCl(s)\,|\,KCl\,(soln)\,|\,AgNO_3\,(soln)\,|\,Ag$
(b) $Pt\,|\,H_2(g)\,|\,HCl\,(soln)\,|\,AgNO_3\,(soln)\,|\,Ag$
(c) $Pt\,|\,H_2(g)\,|\,HCl\,(soln)\,|\,AgCl(s)\,|\,Ag$
(d) $Pt\,|\,H_2(g)\,|\,KCl\,(soln)\,|\,AgCl(s)\,|\,Ag$

16. A solution containing one mole per litre of each $Cu(NO_3)_2$; $AgNO_3$; $Hg_2(NO_3)_2$; is being electrolysed by using inert electrodes. The values of standard electrode potentials in volts (reduction potentials) are : **[1984 - 1 Mark]**
$Ag/Ag^+ = +0.80,\ 2Hg/Hg_2^{++} = +0.79$
$Cu/Cu^{++} = +0.34,\ Mg/Mg^{++} = -2.37$
With increasing voltage, the sequence of deposition of metals on the cathode will be :
(a) Ag, Hg, Cu, Mg (b) Mg, Cu, Hg, Ag
(c) Ag, Hg, Cu (d) Cu, Hg, Ag

17. The standard reduction potentials at 298 K for the following half reactions are given against each **[1981 - 1 Mark]**
$Zn^{2+}(aq) + 2e \rightleftharpoons Zn(s) \quad -0.762$
$Cr^{3+}(aq) + 2e \rightleftharpoons Cr(s) \quad -0.740$
$2H^+(aq) + 2e \rightleftharpoons H_2(g) \quad 0.000$
$Fe^{3+}(aq) + 2e \rightleftharpoons Fe^{2+}(aq) \quad 0.770$
which is the strongest reducing agent?
(a) Zn(s) (b) Cr(s)
(c) $H_2(g)$ (d) Fe^{2+} (aq)

2 Integer Value Answer

18. For the electrochemical cell, **[Adv. 2018]**
$Mg(s)\,|\,Mg^{2+}\,(aq, 1\ M)\,||\,Cu^{2+}\,(aq, 1\ M)\,|\,Cu(s)$
the standard emf of the cell is 2.70 V at 300 K. When the concentration of Mg^{2+} is changed to *x* M, the cell potential changes to 2.67 V at 300 K. The value of *x* is__________.

(given, $\frac{F}{R} = 11500\ \text{K V}^{-1}$, where F is the Faraday constant and R is the gas constant, ln 10=2.30)

19. All the energy released from the reaction $X \to Y, \Delta_r G^\circ = -193\ \text{kJ mol}^{-1}$ is used for oxidizing M^+ as $M^+ \to M^{3+} + 2e^-$, $E^\circ = -0.25$ V

Under standard conditions, the number of moles of M^+ oxidized when one mole of X is converted to Y is
[F = 96500 C mol^{-1}] **[Adv. 2015]**

3 Numeric / New Stem Based Questions

20. The reduction potential (E^0, in V) of $\text{MnO}_4^-(\text{aq})/\text{Mn(s)}$ is ______. **[Adv. 2022]**

[Given: :

$$[E^0_{(\text{MnO}_4^-(\text{aq})/\text{MnO}_{2(s)})} = 1.68\ \text{V};\ E^0_{(\text{MnO}_2(\text{s})/\text{Mn}^{2+}{}_{(\text{aq})})} = 1.21\ \text{V};$$

$$E^0_{(\text{Mn}^{2+}{}_{(\text{aq})}/\text{Mn}_{(\text{s})})} = -1.03\ \text{V}]$$

21. Consider an electrochemical cell:
$A(\text{s})\,|\,A^{n+}(\text{aq}, 2\ \text{M})\,|B^{2n+}(\text{aq}, 1\ \text{M})\,|\,B(\text{s})$.
The value of ΔH° for the cell reaction is twice that of ΔG° at 300 K. If the emf of the cell is zero, the ΔS° (in J K^{-1} mol^{-1}) of the cell reaction per mole of B formed at 300 K is ______.
(Given: ln(2) = 0.7, R (universal gas constant) = 8.3 J K^{-1} mol^{-1}. H, S and G are enthalpy, entropy and Gibbs energy, respectively.) **[Adv. 2018]**

22. Two students use same stock solution of $ZnSO_4$ and a solution of $CuSO_4$. The emf of one cell is 0.03 V higher than the other. The conc. of $CuSO_4$ in the cell with higher emf value is 0.5 M. Find out the conc. of $CuSO_4$ in the other cell (2.203 RT/F = 0.06). **[2003 - 2 Marks]**

23. The standard reduction potential for $Cu^{2+}|Cu$ is +0.34 V. Calculate the reduction potential at pH = 14 for the above couple. K_{sp} of $Cu(OH)_2$ is 1.0×10^{-19} **[1996 - 3 Marks]**

24. An excess of liquid mercury is added to an acidified solution of 1.0×10^{-3} M Fe^{3+}. It is found that 5% of Fe^{3+} remains at equilibrium at 25°C. Calculate $E^\circ_{Hg_2^{2+}|Hg}$, assuming that the only reaction that occurs is

$$2Hg + 2Fe^{3+} \longrightarrow Hg_2^{2+} + 2Fe^{2+}.$$

(Given $E^\circ_{Fe^{3+}|Fe^{2+}} = 0.77\ \text{V}$.) **[1995 - 4 Marks]**

4 Fill in the Blanks

25. The more .... the standard reduction potential, the .... is its ability to displace hydrogen from acids. **[1986 - 1 Mark]**

5 True / False

26. The dependence of electrode potential for the electrode M^{n+}/M with concentration under STP conditions is given by the expression: $E = E^\circ + \frac{0.0591}{n}\log_{10}[M^{n+}]$ **[1993 - 1 Mark]**

6 MCQs with One or More than One Correct Answer

27. The correct option(s) about entropy (S) is(are)
[R = gas constant, F = Faraday constant, T = Temperature] **[Adv. 2022]**

(a) For the reaction, $M(s) + 2H^+(aq) \to H_2(g) + M^{2+}(aq)$, if $\frac{dE_{cell}}{dT} = \frac{R}{F}$, then the entropy change of the reaction is R (assume that entropy and internal energy changes are temperature independent).

(b) The cell reaction, $Pt(s)\,|\,H_2(g, 1\text{bar})\,|\,H^+(aq, 0.01\text{M})\,\|\,H^+(aq, 0.1\text{M})\,|\,H_2(g, 1\text{bar})\,|\,Pt(s)$, is an entropy driven process.

(c) For racemization of an optically active compound, $\Delta S > 0$.

(d) $\Delta S > 0$, for $[Ni(H_2O)_6]^{2+} + 3\,en \to [Ni(en)_3]^{2+} + 6H_2O$ (where en = ethylenediamine).

28. Some standard electrode potentials at 298 K are given below: **[Adv. 2021]**

Pb^{2+}/Pb	−0.13 V
Ni^{2+}/Ni	−0.24 V
Cd^{2+}/Cd	−0.40 V
Fe^{2+}/Fe	−0.44 V

To a solution containing 0.001 M of X^{2+} and 0.1 M of Y^{2+}, the metal rods X and Y are inserted (at 298 K) and connected by a conducting wire. This resulted in dissolution of X. The correct combination(s) of X and Y, respectively, is (are)
(Given: Gas constant, R = 8.314 J K^{-1} mol^{-1}, Faraday constant, F = 96500 C mol^{-1})

(a) Cd and Ni (b) Cd and Fe
(c) Ni and Pb (d) Ni and Fe

29. In a galvanic cell, the salt bridge **[Adv. 2014]**

(a) Does not participate chemically in the cell reaction
(b) Stops the diffusion of ions from one electrode to another
(c) Is necessary for the occurrence of the cell reaction
(d) Ensures mixing of the two electrolytic solutions

30. For the reduction of NO_3^- ion in an aqueous solution, E° is + 0.96V. Values of E° for some metal ions are given below

$V^{2+}(aq) + 2e^- \to V$ $E^\circ = -1.19$ V
$Fe^{3+}(aq) + 3e^- \to Fe$ $E^\circ = -0.04$ V
$Au^{3+}(aq) + 3e^- \to Au$ $E^\circ = +1.40$ V
$Hg^{2+}(aq) + 2e^- \to Hg$ $E^\circ = +0.86$ V

The pair(s) of metals that is (are) oxidized by NO_3^- in aqueous solution is (are) **[2009]**

(a) V and Hg (b) Hg and Fe
(c) Fe and Au (d) Fe and V

31. The standard reduction potential values of three metallic cations, X, Y and Z are 0.52, −3.03 and −1.18 V respectively. The order of reducing power of the corresponding metals is **[1998 - 2 Marks]**

(a) $Y > Z > X$ (b) $X > Y > Z$
(c) $Z > Y > X$ (d) $Z > X > Y$

7 Match the Following

32. The standard reduction potential data at 25°C is given below : **[Adv. 2013]**

$E°(Fe^{3+}, Fe^{2+}) = +0.77\ V; E°(Fe^{2+}, Fe) = -0.44\ V; E°(Cu^{2+}, Cu) = +0.34\ V; E°(Cu^{+}, Cu) = +0.52\ V$

$E°[O_2(g) + 4H^+ + 4e^- \rightarrow 2H_2O] = +1.23\ V; E°[O_2(g) + 2H_2O + 4e^- \rightarrow 4OH^-] = +0.40\ V$

$E°(Cr^{3+}, Cr) = -0.74\ V; E°(Cr^{2+}, Cr) = -0.91\ V$

Match $E°$ of the redox pair in List-I with the values given in List-II and select the correct answer using the code given below the lists:

List-I		List-II	
P.	$E°(Fe^{3+}, Fe)$	1.	$-0.18\ V$
Q.	$E°(4H_2O \rightleftharpoons 4H^+ + 4OH^-)$	2.	$-0.4\ V$
R.	$E°(Cu^{2+} + Cu \rightarrow 2Cu^+)$	3.	$-0.04\ V$
S.	$E°(Cr^{3+}, Cr^{2+})$	4.	$-0.83\ V$

Codes :

	P	Q	R	S
(a)	4	1	2	3
(b)	2	3	4	1
(c)	1	2	3	4
(d)	3	4	1	2

8 Comprehension/Passage Based Questions

Passage-I

The electrochemical cell shown below is a concentration cell.
$M \mid M^{2+}$ (saturated solution of a sparingly soluble salt, MX_2) $\| M^{2+}$ (0.001 mol dm^{-3}) $\mid M$.

The emf of the cell depends on the difference in concentrations of M^{2+} ions at the two electrodes. The emf of the cell at 298 K is 0.059 V. **[2012]**

33. The value of ΔG (kJ mol^{-1}) for the given cell is (take 1F = 96500 C mol^{-1})
(a) –5.7 (b) 5.7 (c) 11.4 (d) –11.4

Passage-II

The concentration of potassium ions inside a biological cell is atleast twenty times higher than the outside. The resulting potential difference across the cell is important in several processes such as transmission of nerve impulses and maintaining the ion balance. A simple model for such a concentration cell involving a metal M is

$M(s) \mid M^+(aq; 0.05\ \text{molar}) \| M^+(aq; 1\ \text{molar}) \mid M(s)$

For the above electrolytic cell the magnitude of the cell potential $|E_{cell}| = 70\ mV$. **[2010]**

34. For the above cell
(a) $E_{cell} < 0; \Delta G > 0$ (b) $E_{cell} > 0; \Delta G < 0$
(c) $E_{cell} < 0; \Delta G° > 0$ (d) $E_{cell} > 0; \Delta G° < 0$

35. If the 0.05 molar solution of M^+ is replaced by a 0.0025 molar M^+ solution, then the magnitude of the cell potential would be
(a) 35mV (b) 70mV (c) 140mV (d) 700mV

Passage: III

Redox reactions play a pivotal role in chemistry and biology. The values of standard redox potential ($E°$) of two half-cell reactions decide which way the reaction is expected to proceed. A simple example is a Daniell cell in which zinc goes into solution and copper gets deposited. Given below are a set of half-cell reactions (acidic medium) along with their $E°$ (V with respect to normal hydrogen electrode) values. Using this data, obtain the correct explanations to questions given. **[2007]**

$I_2 + 2e^- \rightarrow 2I^-$ $E° = 0.54$
$Cl_2 + 2e^- \rightarrow 2Cl^-$ $E° = 1.36$
$Mn^{3+} + e^- \rightarrow Mn^{2+}$ $E° = 1.50$
$Fe^{3+} + e^- \rightarrow Fe^{2+}$ $E° = 0.77$
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ $E° = 1.23$

36. Among the following, identify the correct statement.
(a) Chloride ion is oxidised by O_2
(b) Fe^{2+} is oxidised by iodine
(c) Iodide ion is oxidised by chlorine
(d) Mn^{2+} is oxidised by chlorine

37. While Fe^{3+} is stable, Mn^{3+} is not stable in acid solution because
(a) O_2 oxideses Mn^{2+} to Mn^{3+}
(b) O_2 oxideses both Mn^{2+} to Mn^{3+} and Fe^{2+} to Fe^{3+}
(c) Fe^{3+} oxideses H_2O to O_2
(d) Mn^{3+} oxideses H_2O to O_2

38. Sodium fusion extract, obtained from aniline, on treatment with iron (II) sulphate and H_2SO_4 in presence of air gives a Prussian blue precipitate. The blue colour is due to the formation of
(a) $Fe_4[Fe(CN)_6]_3$ (b) $Fe_3[Fe(CN)_6]_2$
(c) $Fe_4[Fe(CN)_6]_2$ (d) $Fe_3[Fe(CN)_6]_3$

Passage-IV

Tollen's test is given by aldehydes.

$$Ag^+ + e^- \longrightarrow Ag;\ E°_{red} = +0.800\ V$$

$$\underset{\text{Gluconic acid}}{C_6H_{12}O_6 + H_2O \longrightarrow C_6H_{12}O_7} + 2H^+ + 2e^-;\ E°_{ox} = -0.05V$$

$$[Ag(NH_3)_2]^+ + e^- \longrightarrow Ag + 2NH_3;\ E°_{red} = 0.373V$$

Given $\frac{2.303RT}{F} = 0.0591$ & $\left(\frac{F}{RT}\right) = 38.92V^{-1}$

39. Calculate (ln K) for **[2006 - 5M, –2]**

$$C_6H_{12}O_6 + 2Ag^+ + H_2O \longrightarrow C_6H_{12}O_7 + 2H^+ + 2Ag$$

(a) 55.6 (b) 29.6 (c) 66 (d) 58.38

40. On adding NH_3, pH of the solution increases to 11 then, identify the effect on potential of half-cell **[2006 - 5M, –2]**
(a) E_{ox} increased from $E°_{ox}$ by 0.65 V
(b) E_{ox} decreased from $E°_{ox}$ by 0.65 V
(c) E_{red} increased from $E°_{red}$ by 0.65 V
(d) E_{red} decreased from $E°_{red}$ by 0.65 V

41. NH_3 is used in this reaction rather than any other base. Select the correct statement out of the following **[2006 - 5M, –2]**

(a) $[Ag(NH_3)_2]^+$ is a weaker oxidizing agent than Ag^+

(b) to dissolve the insoluble silver oxide formed under the reaction conditions

(c) Ag precipitates gluconic acid as its silver salt

(d) NH_3 changes the standard reduction potential of $[Ag(NH_3)_2]^+$

10 Subjective Problems

42. (a) For the reaction

$$Ag^+(aq) + Cl^-(aq) \rightleftharpoons AgCl(s)$$

Given :

Species	ΔG_f° (kJ/mol)
Ag^+ (aq)	+77
Cl^- (aq)	– 129
AgCl (s)	– 109

Write the cell representation of above reaction and calculate E°_{cell} at 298 K. Also find the solubility product of AgCl.

(b) If 6.539×10^{-2} g of metallic zinc is added to 100 mL saturated solution of AgCl. Find the value of

$$\log_{10} \frac{[Zn^{2+}]}{[Ag^+]^2}.$$

How many moles of Ag will be precipitated in the above reaction. Given that **[2005 - 6 Marks]**

$Ag^+ + e^- \longrightarrow Ag$; $E^\circ = 0.80$ V ;

$Zn^{2+} + 2e^- \longrightarrow Zn$; $E^\circ = -0.76$ V

(It was given that Atomic mass of Zn = 65.39)

43. Find the equilibrium constant for the reaction,

$$In^{2+} + Cu^{2+} \longrightarrow In^{3+} + Cu^+ \text{ at } 298\text{ K}$$

given : $E^\circ_{Cu^{2+}/Cu^+} = 0.15$ V; $E^\circ_{In^{2+}/In^+} = -0.40$ V,

$E^\circ_{In^{3+}/In^+} = -0.42$ V **[2004 - 4 Marks]**

44. The standard potential of the following cell is 0.23 V at 15°C and 0.21 V at 35°C. **[2001 - 10 Marks]**

$Pt \mid H_2(g) \mid HCl(aq) \mid AgCl(s) \mid Ag(s)$

(*i*) Write the cell reaction.

(*ii*) Calculate ΔH° and ΔS° for the cell reaction by assuming that these quantities remain unchanged in the range 15°C to 35°C.

(*iii*) Calculate the solubility of AgCl in water at 25°C.

Given : The standard reduction potential of the $Ag^+(aq) / Ag(s)$ couple is 0.80 V at 25°C.

45. The following electrochemical cell has been set up.

$Pt(1) \mid Fe^{3+}, Fe^{2+} (a = 1) \mid Ce^{4+}, Ce^{3+} (a = 1) \mid Pt(2)$

$E^\circ (Fe^{3+}, Fe^{2+}) = 0.77$ V : $E^\circ (Ce^{4+} / Ce^{3+}) = 1.61$ V

If an ammeter is connected between the two platinum electrodes, predict the direction of flow of current. Will the current increase or decrease with time? **[2000 - 2 Marks]**

46. A cell, $Ag \mid Ag^+ \| Cu^{2+} \mid Cu$, initially contains 1 M Ag^+ and 1 M Cu^{2+} ions. Calculate the change in the cell potential after the passage of 9.65 A of current for 1 h.

[1999 - 6 Marks]

47. Find the solubility product of a saturated solution of Ag_2CrO_4 in water at 298 K if the emf of the cell $Ag \mid Ag^+$ (satd. Ag_2CrO_4 soln.) $\| Ag^+(0.1M) \mid Ag$ is 0.164 V at 298 K.

[1998 - 6 Marks]

48. Calculate the equilibrium constant for the reaction, $2Fe^{3+} + 3I^- \rightleftharpoons 2Fe^{2+} + I_3^-$. The standard reduction potentials in acidic conditions are 0.77 V and 0.54 V respectively for $Fe^{3+} \mid Fe^{2+}$ and $I_3^- \mid I^-$ couples. **[1998 - 3 Marks]**

49. Calculate the equilibrium constant for the reaction

$Fe^{2+} + Ce^{4+} \rightleftharpoons Fe^{3+} + Ce^{3+}$ **[1997 - 2 Marks]**

(given $E^\circ_{Ce^{4+}/Ce^{3+}} = 1.44$ V; $E^\circ_{Fe^{3+}/Fe^{2+}} = 0.68$ V;)

50. Although aluminium is above hydrogen in the electrochemical series, it is stable in air and water. Explain.

[1994 - 1 Mark]

51. The Edison storage cells is represented as

$Fe(s) \mid FeO(s) \mid KOH(aq) \mid Ni_2O_3(s) \mid Ni(s)$

The half-cell reactions are :

$$Ni_2O_3(s) + H_2O(l) + 2e^- \rightleftharpoons 2NiO_{(s)} + 2OH^- ; \quad E^\circ = +0.40\text{V}$$

$$FeO(s) + H_2O(l) + 2e^- \rightleftharpoons Fe(s) + 2OH^- ; E^\circ = -0.87\text{V}$$

(*i*) What is the cell reaction ?

(*ii*) What is the cell e.m.f ? How does it depend on the concentration of KOH?

(*iii*) What is the maximum amount of electrical energy that can be obtained from one mole of Ni_2O_3?

[1994 - 4 Marks]

52. The standard reduction potential of the Ag^+ / Ag electrode at 298 K is 0.799 V. Given that for AgI, $K_{sp} = 8.7 \times 10^{-17}$, evaluate the potential of the Ag^+/Ag electrode in a saturated solution of AgI. Also calculate the standard reduction potential of the $I^- / AgI / Ag$ electrode.

[1994 - 3 Marks]

53. The standard reduction potential for the half-cell

$NO_3^-(aq) + 2H^+(aq) + e \rightarrow NO_2(g) + H_2O$ is 0.78 V.

(i) Calculate the reduction potential in 8 M H^+

(ii) What will be the reduction potential of the half-cell in a neutral solution? Assume all the other species to be at unit concentration. **[1993 - 2 Marks]**

54. An aqueous solution of NaCl on electrolysis gives $H_2(g)$, $Cl_2(g)$ and NaOH according to the reaction :

$2Cl^-(aq) + 2H_2O = 2OH^-(aq) + H_2(g) + Cl_2(g)$.

A direct current of 25 amperes with a current efficiency of 62% is passed through 20 litres of NaCl solution (20% by weight). Write down the reactions taking place at the anode and the cathode. How long will it take to produce 1 kg of Cl_2? What will be the molarity of the solution with respect to hydroxide ion? (Assume no loss due to evaporation.)

[1992 - 3 Marks]

55. For the galvanic cell. **[1992 - 4 Marks]**
$Ag \mid AgCl(s), KCl(0.2\,M) \parallel KBr\,(0.001M), AgBr(s) \mid Ag$
Calculate the EMF generated and assign correct polarity to each electrode for a spontaneous process after taking into account the cell reaction at 25°C.
$[K_{sp}(AgCl) = 2.8 \times 10^{-10}; K_{sp}(AgBr) = 3.3 \times 10^{-13}]$

56. Zinc granules are added in excess to a 500 mL. of 1.0 M nickel nitrate solution at 25°C until the equilibrium is reached. If the standard reduction potential of $Zn^{2+} \mid Zn$ and $Ni^{2+} \mid Ni$ are –0.75 V and –0.24 V respectively, find out the concentration of Ni^{2+} in solution at equilibrium. **[1991 - 2 Marks]**

57. The standard reduction potential of Cu^{++}/Cu and Ag^{+}/Ag electrodes are 0.337 and 0.799 volt respectively. Construct a galvanic cell using these electrodes so that its standard e.m.f. is positive. For what concentration of Ag^{+} will the e.m.f. of the cell, at 25°C, be zero if the concentration of Cu^{++} is 0.01 M? **[1990 - 3 Marks]**

58. The standard reduction potential at 25°C of the reaction, $2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^-$ is –0.8277V. Calculate the equilibrium constant for the reaction $2H_2O \rightleftharpoons H_3O^+ + OH^-$ at 25°C. **[1989 - 3 Marks]**

59. A cell contains two hydrogen electrodes. The negative electrode is in contact with a solution of 10^{-6} M hydrogen ions. The EMF of the cell is 0.118 V at 25°C. Calculate the concentration of hydrogen ions at the positive electrode. **[1988 - 2 Marks]**

60. The EMF of a cell corresponding to the reaction :
$Zn(s) + 2H^+(aq) \rightarrow Zn^{2+} + (0.1\ M) + H_2\,(g)\,(1\ atm.)$
is 0.28 volt at 25°C.
Write the half-cell reactions and calculate the pH of the solution at the hydrogen electrode.
$E^{\circ}_{Zn^{2+}/Zn} = -0.76$ volt; $E^{\circ}_{H^+/H_2} = 0$ **[1986 - 4 Marks]**

61. Consider the cell **[1982 - 2 Marks]**
$Zn \mid Zn^{2+}\,(aq)\,(1.0\,M) \parallel Cu^{2+}\,(aq)\,(1.0\,M) \mid Cu.$
The standard reduction potentials are :
+0.350 volts for $2e^- + Cu^{2+}(aq) \rightarrow Cu$ and –0.763 volts for $2e^- + Zn^{2+}(aq) \rightarrow Zn$
(i) Write down the cell reaction.
(ii) Calculate the emf of the cell.
(iii) Is the cell reaction spontaneous or not?

62. (a) 19 g of molten $SnCl_2$ is electrolysed for some time. Inert electrodes are used. 0.119 g of Sn is deposited at the cathode. No substance is lost during the electrolysis. Find the ratio of the weights of $SnCl_2$: $SnCl_4$ after electrolysis.
(b) A hot solution of NaCl in water is electrolysed. Iron electrodes are used. Diaphragm cell is not used. Give equations for all the chemical reactions that take place during electrolysis.
(c) Find the charge in coulombs of 1 gram ion of N^{3-}. **[1980]**

AnswerKey

Topic-1 : Conductance of Electrolytic Solution and Electrolysis

1. (a) **2.** (d) **3.** (d) **4.** (b) **5.** (b) **6.** (d) **7.** (c) **8.** (7) **9.** (6) **10.** (3)
11. (0.22) **12.** (0.86) **13.** (13.32) **14.** (0.154) **15.** (19.06) **16.** (125.09) **17.** (27171.96) **18.** (increased)
19. (a, c) **20.** (c) **21.** (a) **22.** (i)-(s); (ii)-(r); (iii)-(q); (iv)-(p) **23.** (b) **24.** (d) **25.** (d)

Topic-2 : Nernst Equation, Commercial Cells and Corrosion

1. (b) **2.** (d) **3.** (d) **4.** (a) **5.** (b) **6.** (c) **7.** (a) **8.** (c) **9.** (b) **10.** (a)
11. (c) **12.** (a) **13.** (b) **14.** (a) **15.** (c) **16.** (c) **17.** (a) **18.** (10) **19.** (4) **20.** (0.77)
21. (–11.62) **22.** (0.05) **23.** (–0.22) **24.** (0.792) **25.** (negative, greater) **26.** (False) **27.** (b, c, d) **28.** (a, b, c)
29. (a) **30.** (a,b,d) **31.** (a) **32.** (d) **33.** (d) **34.** (b) **35.** (c) **36.** (c) **37.** (d) **38.** (a)
39. (d) **40.** (a) **41.** (b)

Hints & Solutions

Topic-1: Conductance of Electrolytic Solution and Electrolysis

1. (a) For weak acid, $\alpha = \frac{\Lambda_m}{\Lambda_0}$

$$K_a \frac{c\alpha^2}{1-\alpha} \Rightarrow K_a(1-\alpha) = c\alpha^2$$

$$\Rightarrow K_a\left(1-\frac{\Lambda_m}{\Lambda_0}\right) = c\left(\frac{\Lambda_m}{\Lambda_0}\right)^2$$

$$\Rightarrow K_a - \frac{\Lambda_m K_a}{\Lambda_0} = \frac{c\Lambda_m^2}{(\Lambda_0)^2} \Rightarrow K_a = \frac{c\Lambda_m^2}{(\Lambda_0)^2} + \frac{\Lambda_m K_a}{\Lambda_0}$$

Divide by 'Λ_m'

$$\Rightarrow \frac{K_a}{\Lambda_m} = \frac{c\Lambda_m}{(\Lambda_0)^2} + \frac{K_a}{\Lambda_0} \Rightarrow \frac{1}{\Lambda_m} = \frac{c\Lambda_m}{K_a(\Lambda_0)^2} + \frac{1}{\Lambda_0}$$

For the Plot $\frac{1}{\Lambda_m}$ vs $c\Lambda_m$, Slope $= \frac{1}{K_a(\Lambda_0)^2} = S$

$$\text{y–intercept} = \frac{1}{\Lambda_0} = P \quad \therefore \quad \frac{P}{S} = \frac{\frac{1}{\Lambda_0}}{\frac{1}{K_a(\Lambda_0)^2}} = K_a\Lambda_0$$

2. (d) Sodium stearate at low concentration (*i.e.*, below CMC) behaves as normal strong electrolyte, but at higher concetration (*i.e.* above CMC) exhibits colloidal behaviour due to the formation of micelles. Thus, plot (d) correctly represents relation between Λ_m and $\sqrt{C}$ for sodium strearate.

3. (d) $AgNO_3(aq) + KCl(aq) \longrightarrow AgCl(s) + KNO_3(aq)$ Conductivity of the solution is almost compensated due to formation of $KNO_3(aq)$. However, after end point, conductivity increases more rapidly due to addition of excess $AgNO_3$ solution.

4. (b) Give : $I = 10$ milliamperes ; $F = 96500\ C\ mol^{-1}$

$t = ?$; Moles of H_2 produces $= 0.01$ mol

From the law of electrolysis, we have

$$\text{Equivalents of } H_2 \text{ produces} = \frac{I \times t(\text{sec})}{96500}$$

Substituting given values, we get

$$0.01 \times 2 = \frac{10 \times 10^{-3}(\text{amperes}) \times t(\text{sec})}{96500} = 19.3 \times 10^4 \text{sec.}$$

5. (b) As we go down the group 1 (*i.e.* from Li^+ to K^+), the ionic radius increases, degree of solvation decreases and hence effective size decreases resulting in increase in ionic mobility. Hence, equivalent conductance at infinite dilution increases in the same order.

6. (d) Charge of one mole of electrons = 96500 C $\therefore$ 1 gram equivalent of substance will be deposited by one mole of electrons.

7. (c) $\frac{W_1}{W_2} = \frac{E_1}{E_2} = \frac{Z_1 it}{Z_2 it} \quad \therefore \quad \frac{Z_1}{Z_2} = \frac{E_1}{E_2}$

Here E_1 & E_2 are equivalent weights of the ions.

8. (7)

$$\Lambda^\circ(U_mY_P) = m\lambda^\circ(U^{P+}) + p\lambda^\circ(Y^{m-})$$

$$\Rightarrow 25m + 100p = 250$$

$$\Rightarrow m + 4p = 10 \quad \text{...(1)}$$

$$\Lambda^\circ(V_mX_n) = m\lambda^\circ(V^{n+}) + n\lambda^\circ(X^{m-})$$

$$\Rightarrow 100m + 80n = 440$$

$$\Rightarrow 5m + 4n = 22 \quad \text{...(2)}$$

For electrolyte Z_mX_n from the given curve,

$$\Lambda(Z_mX_n) = \Lambda^\circ(Z_mX_n) - A\sqrt{C}$$

$$\text{Slope, } m = -A = \frac{339-336}{0.01-0.04}$$

$$\Rightarrow A = 100$$

For $\lambda_m = 339\ S\ cm^2\ mol^{-1}$, $\sqrt{C} = 0.01\ (mol\ L^{-1})^{1/2}$

$$339 = \Lambda^\circ(Z_mX_n) - 100 \times 0.01$$

$$\Rightarrow \Lambda^\circ(Z_mX_n) = 340\ S\ cm^2\ mol^{-1}$$

$$\Rightarrow m\lambda^\circ(Z^{n+}) + n\lambda^\circ(Z^{m-}) = 340$$

$$\Rightarrow 50m + 80n = 340$$

$$\Rightarrow 5m + 8n = 34 \quad \text{... (3)}$$

From eq. (2) and (3),

n = 3 and m = 2

Putting value of m in eq. (1),

p = 2

Therefore, m + n + p = 2 + 3 + 2 = 7.

9. (6) The formula for conductance is $G = \kappa \times \frac{a}{l}$

$$5 \times 10^{-7} = \kappa \times \frac{1}{120} = 6 \times 10^{-5}\ S\ cm^{-1}$$

$$\Lambda_m^c = \frac{\kappa \times 1000}{M} = \frac{6 \times 10^{-5} \times 1000}{0.0015} = 40$$

$\because$ pH = 4

$$\therefore\ [H^+] = 10^{-4} = c\alpha = 0.0015\,\alpha\ ;\ \alpha = \frac{10^{-4}}{0.0015}$$

Also, $\alpha = \dfrac{\Lambda_m^c}{\Lambda_m^o} \Rightarrow \dfrac{10^{-4}}{0.0015} = \dfrac{40}{\Lambda_m^o}$

$$\Lambda_m^o = \frac{40\times 0.0015}{10^{-4}} = 6\times 10^2\,\text{S cm}^2\ \text{mol}^{-1};\ Z \approx 6$$

10. **(3)** $1 \rightarrow HX$ $\qquad 2 \rightarrow HY$

$$\alpha_1 = \frac{(\lambda_m)_{HX}}{\overset{\circ}{\lambda}_m} \qquad \alpha_2 = \frac{(\lambda_m)_{HY}}{\overset{\circ}{\lambda}_m}$$

$$\begin{array}{cccc} HX & \rightleftharpoons & H^+ & + & X^- \\ 1 & & 0 & & 0 \\ (1-\alpha)C_1 & & \alpha_1 C_1 & & \alpha_1 C_1 \end{array}$$

$$K_{a_1} = \frac{\alpha_1^2 C_1}{1-\alpha_1}\ [\because \alpha \ll 1\ \therefore\ 1-\alpha_1 \approx 1]$$

$$\therefore\ K_{a_1} = \alpha_1^2 C_1^2;\ K_{a_2} = \alpha_2 C_2$$

$$K_{a_1} = C_1\alpha_1^2;\ K_{a_2} = C_2\alpha_2^2$$

$$= 0.01\frac{(\lambda_m)^2_{HX}}{\left(\overset{\circ}{\lambda}_m\right)^2} = 0.1\frac{(\lambda_m)^2{}_{HY}}{\left(\overset{\circ}{\lambda}_m\right)^2}$$

$$\therefore\quad \frac{K_{a_1}}{K_{a_2}} = \frac{0.01(\lambda_m)^2_{HX}}{0.1(\lambda_m)^2_{HY}} = 0.1\left(\frac{(\lambda_m)_{HX}}{(\lambda_m)_{HY}}\right)^2$$

$$= 0.1\left(\frac{1}{10}\right)^2 = 10^{-3}$$

$$pK_a(HX) - pK_a(HY) = -\log\frac{K_{a_1}}{K_{a_2}} = -\log 10^{-3} = 3$$

11. **(0.22)**

$$K_a = \frac{\Lambda_m^2 C}{\overset{\circ}{\Lambda}_m(\overset{\circ}{\Lambda}_m - \Lambda_m)} = \frac{(y\times 10^2)^2\times C}{4\times 10^2(4\times 10^2 - y\times 10^2)}$$

$$= \frac{(3y\times 10^2)^2\times \frac{C}{20}}{4\times 10^2(4\times 10^2 - 3y\times 10^2)} \Rightarrow y = \frac{44}{51}$$

$$\therefore\quad \Lambda_m = \frac{44}{51}\times 10^2\ \text{S cm}^2\ \text{mol}^{-1}$$

$$\alpha = \frac{\frac{44}{51}\times 10^2}{4\times 10^2} = 0.2156\ (\alpha = 0.22 \text{ or } 0.21)$$

12. **(0.86)**

13. **(13.32)**

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$$

$E^0{}_{cell} = 1.23 - 0.00 = 1.23\ \text{V}$

$\Delta G^0{}_{cell} = -nF\,E^0{}_{cell} = -2\times 96500\times 1.23\ \text{J}$

$\therefore$ Work derived from this fuel cell using 70% efficiency

$$= \frac{70}{100}\times\left(-\Delta G^0_{cell}\right)\times 10^{-3}$$

$$= 0.7\times 2\times 96500\times 1.23\times 10^{-3} = 166.17\ \text{J}$$

For insulated vessel, $q = 0$

Therefore for monoatomic gas,

$w = \Delta U$

$166.17 = nC_{v,m}\Delta T;\ \therefore\ \Delta T = 13.32\text{K}$

14. **(0.154)** $i = \dfrac{1.70\times 90}{100}$ ampere

No. of equivalents of Zn^{2+} which are lost

$$= \frac{i\times t}{96500} = \frac{1.70\times 90\times 230}{100\times 96500} = 3.646\times 10^{-3}$$

$\therefore$ Milli equivalents of Zn^{2+} which are lost 3.646

$\therefore$ Initial value of $Zn^{2+} = 300\times 0.160\times 2 = 96$

$\therefore$ Mili equivalents of Zn^{2+} left in solution

$= 96 - 3.646 = 92.354$

$$[ZnSO_4] = \frac{92.354}{2\times 300} = 0.154\ \text{M}$$

15. **(19.06)**

Watt = Volt × Current $\Rightarrow 100 = 110\times$ Current

or $\quad$ Current $= \dfrac{100}{110} = \dfrac{10}{11}$ amp.

Now we know that,

$$Q = i\times t = \frac{10}{11}\times 10\times 3600\times\frac{1}{96500} = 0.339\ \text{F}$$

Wt. of cadmium deposited $= \dfrac{0.339\times 112.4}{2} = \mathbf{19.06\ g}$

16. **(125.09)** Volume of the surface = area × thickness

$$= 80\ \text{cm}^2\times\frac{0.005}{10}\ \text{cm} = \frac{1}{25}\ \text{cm}^3$$

Mass of Ag deposited = Volume × Density

$$= \frac{1}{25}\times 10.5\ \text{g/cm}^3 = \frac{21}{50}\ \text{g}$$

Cell reaction : $Ag^+ + e^- \rightarrow\ Ag$

We know that, $\dfrac{W}{E} = \dfrac{Q}{F} = \dfrac{it}{F}$

E = Eq. wt. of Ag $= 108\ \therefore\ \dfrac{21/50}{108} = \dfrac{i\times t}{96500}$

$$\frac{21}{50\times 108} = \frac{3\times t}{96500}\quad\therefore\ t = \mathbf{125.09\ sec}$$

17. **(27171.96)** Wt. of Cu deposited = Zit

Electrochemical equivalent of Cu $= \frac{63.5}{2} = 31.75$

Volume of surface = area × thickness

$= 10 \times 10 \times 10^{-2} = 1$ cc

Weight of Cu = density × volume $= 8.94 \times 1 = 8.94$ g

According to Faraday's laws of electrolysis

31.75 g of Cu is deposited by = 96500 coulombs of electricity

$\therefore$ 8.94 g of Cu is deposited by $= \frac{96500}{31.75} \times 8.94$

$= \mathbf{27171.96\ coulombs}$

18. **increased;** Formed salt will be a strong electrolyte.

19. **(a, c)** $\underset{\substack{\text{Oxidation}\\\text{(anode)}}}{\overset{-2}{N_2H_4}} + \underset{\substack{\text{Reduction}\\\text{(cathode)}}}{\overset{2}{O_2}} \longrightarrow \overset{0}{N_2} + H_2\overset{-2}{O}$

At anode : $N_2H_4 + 4OH^- \longrightarrow N_2 + 4H_2O + 4e^-$

At cathode : $O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$

Complete reaction : $N_2H_4 + O_2 \longrightarrow N_2 + 2H_2O$

Thus, statements (a) and (c) are correct.

20. **(c)**

(P) $KCl + AgNO_3 \rightarrow AgCl\downarrow + KNO_3$

Cl^- ions is replaced by NO_3^- ions

Conductance will first decrease and then after equivalence point, it will increase P → (3)

(Q) $AgNO_3 + KCl \rightarrow AgCl + KNO_3$

Ag^+ ions is replaced by K^+ ions

Conductance will first increase slightly and then will increase further

(R) $NaOH + HCl \rightarrow NaCl + H_2O$

OH^- ions is replaced by Cl^- ions

(S) $NaOH + CH_3COOH \rightarrow CH_3COONa + H_2O$, OH^- ions is replaced by CH_3COO^-, ions conductance will first decrease and them become almost constant due to buffer formation.

21. **(a)** (P) $\underset{X}{(C_2H_5)_3N} + \underset{Y}{CH_3COOH} \longrightarrow$

$(C_2H_5)_3NH^+CH_3COO^-$

Initially conductivity increases because on neutralisation ions are created. After that it becomes practically constant because X alone cannot form ions.

(Q) $\underset{X}{KI(0.1M)} + \underset{Y}{AgNO_3(0.01M)} \longrightarrow AgI\downarrow + KNO_3$

Number of ions in the solution remains constant as only $AgNO_3$ precipitated as AgI. Thereafter, conductance increases due to increase in number of ions.

(R) Initially conductance decreases due to the decrease in the number of $\overline{O}H$ ions as OH^- is getting replaced by CH_3COO^- which has poorer conductivity. Thereafter, it slowly increases due to the increase in number of H^+ ions.

(S) Initially it decreases due to decrease in H^+ ions and then increases due to the increase in OH^- ions.

22. **(i)-(s); (ii)-(r); (iii)-(q); (iv)-(p)**

23. **(b)** Reaction at anode: $2Cl^- \longrightarrow Cl_2 + 2e^-$

moles of $Cl^- = 4 \times 500 \times 10^{-3} = 2$

moles $Cl_2 = \frac{1}{2} \times 2 = 1$

24. **(d)** 500 mL of 4.0 molar NaCl has 2 mole of NaCl.

By electrolysis, we can get a maximum of 2 moles of sodium which can combine with exactly 2 moles of mercury to give amalgam.

$\therefore$ The maximum weight of amalgam which can be formed from this solution

= weight of 2 mole of sodium + weight of 2 mole of mercury

$= 2 \times 23 + 2 \times 200 = 446$g

25. **(d)** $Na^+ + e^- \longrightarrow Na$

Total number of moles of Na^+ discharged at cathode = 2mole

$\therefore$ The number of electron required for this purpose = 2 mole

$\therefore$ Total charge required

$= 2$ faraday $= 2 \times 96500 = 193000$ coulombs.

26. Given : $\wedge_m^\infty(Ag^+) = 6 \times 10^{-3}$; $\wedge_m^\infty(Br^-) = 8 \times 10^{-3}$;

$\wedge_m^\infty(NO_3^-) = 7 \times 10^{-3}$ and $K_{sp}(AgBr) = 12 \times 10^{-14}$

To find the specific conductivity (κ) of the final solution of AgBr in which $AgNO_3$ (10^{-7} M) is mixed, we must find the individual κ of the ions.

or $\kappa_{soln} = \kappa_{Ag^+} + \kappa_{Br^-} + \kappa_{NO_3^-}$

Again, $\kappa = \wedge_m^\infty \times$ molar concentration

Calculation of molar concentration of ions :

Concentration,

$[NO_3^-] = 10^{-7}$ moles / L $\equiv 10^{-4}$ moles / m^3

Let x be the molar concentration of Ag^+ from AgBr

$\Rightarrow (x + 10^{-7})x = 12 \times 10^{-14}$

or $x^2 + 10^{-7}x - 12 \times 10^{-14} = 0$; $\Rightarrow x = 3 \times 10^{-7}$ M

$\Rightarrow [Br^-] = 3 \times 10^{-7}$ M $\equiv 3 \times 10^{-4}$ moles / m^3 and

$[Ag^+] = 3 \times 10^{-7} + 10^{-7} = 4 \times 10^{-7}$ M $= 4 \times 10^{-4}$ moles / m^3

$\kappa_{Ag^+} = \mathbf{6 \times 10^{-3} \times 4 \times 10^{-4}}$

$= 24 \times 10^{-7}$ (Sm^{2}mol^{-1} × mol / m^3) $= 24 \times 10^{-7}$ S / m.

Similarly, $\kappa_{Br^-} = 8 \times 10^{-3} \times 3 \times 10^{-4} = \mathbf{24 \times 10^{-7}}$ **S/m** and

$$\kappa_{NO_3^-} = 7\times10^{-3}\times10^{-4} = 7\times10^{-7}\ \text{S/m}$$

$$\Rightarrow \kappa = (24+24+7)\times10^{-7}\ \text{S/m} = 55\times10^{-7}\ \text{S/m}$$

So, the correct answer is **55**.

27. $w = Zit$

$$Z \text{ for Cu} = \frac{63.5/2}{96500};\ t = 16\times60 \text{ sec}$$

$$\therefore\ w = \frac{63.5}{2\times96500}\times2\times10^{-3}\times16\times60$$

$$= \frac{63.5\times16\times60\times10^{-3}}{96500}\text{ g}$$

Wt. of Cu at 50% electrolysis of $CuSO_4$

$$= \frac{63.5\times16\times60\times10^{-3}}{96500}\text{ g}$$

Wt. of Cu at 100% electrolysis of $CuSO_4$

$$= \frac{63.5\times2\times16\times60\times10^{-3}}{96500}\text{ g} = 0.198\times63.5\times10^{-4}\text{g}$$

$CuSO_4 \equiv Cu \qquad = 0.198\times10^{-4}$ mol.

$$\therefore \text{ Conc. of } CuSO_4 = 0.198\times10^{-4}\times\frac{1000}{250}$$

$$= \mathbf{7.95\times10^{-5}\ mol/L}$$

28. $$W_{Ag} = \frac{E.i.t}{96500} = \frac{107.8\times8.46\times8\times60\times60}{96500} = \mathbf{34.02g}$$

$$\text{Volume of Ag} = \frac{34.02}{10.5} = 3.24\ \text{cm}^3$$

$$\therefore\ \text{Surface area} = \frac{3.24}{0.00254} = \mathbf{1275.6\,cm^2}$$

29. $CrO_3 + 6H^+ + 6e^- \longrightarrow Cr + 3H_2O$

Eq. wt. of Cr

$$= \frac{\text{At. wt.}}{\text{No. of Electrons lost or gained by one molecule of Cr}}$$

$$= \frac{52}{6}$$

(i) $\because$ 96500 coulomb deposit $= \left(\frac{52}{6}\right)$ g Cr

$$\therefore\ 24000 \text{ coulomb deposit} = \frac{52}{6}\times\frac{24000}{96500}$$

$$= \mathbf{2.1554\ g\ of\ Cr}$$

(ii) Also given, $w_{Cr} = 1.5$ g, $i = 12.5$ ampere, $t = ?$, $E_{Cr} = \frac{52}{6}$

$$\therefore\ w = \frac{Eit}{96500} \text{ or } 1.5 = \frac{52\times12.5\times t}{6\times96500}$$

$\therefore$ $\mathbf{t = 1336.15\ second}$

30. $C_6H_5NO_2 + 6H^+ + 6e^- \longrightarrow C_6H_5NH_2 + 2H_2O$

$$\text{Eq. wt of } C_6H_5NO_2 = \frac{\text{M.wt.}}{6} = \frac{123}{6}$$

$$w = \frac{Eit}{96500};\ i = \frac{50i_0}{100} \qquad \because \text{ current efficiency} = 50\%$$

$$\therefore\ 12.3 = \frac{123\times i\times t\times50}{6\times100\times96500};\ i\times t = Q = \mathbf{115800\ Coulomb}$$

Energy used = 115800 × 3 = **347.4 kJ.**

31. The chemical reactions taking place at the two electrodes are

At cathode : $Cu^{2+} + 2e^- \rightarrow Cu$

$$H_2O \rightleftharpoons H^+ + OH^-$$

Only Cu^{2+} ions will be discharged so as these are present in solution and H^+ ions will be discharged only when all the Cu^{2+} ions have been deposited.

At anode : $2OH^- \rightarrow H_2O + O + 2e^-$

$O + O \rightarrow O_2$

Thus in first case, Cu^{2+} ion will be discharged at the cathode and O_2 gas at the anode. Let us calculate the volume of gas (O_2) discharged during electrolysis.

According to Faraday's second law

31.75 g Cu ≡ 8 g of oxygen ≡ 5.6 litres of O_2 at NTP

$$0.4 \text{ g Cu} = \frac{5.6}{31.75}\times0.4 \text{ litres of } O_2 \text{ at NTP}$$

$$= 0.07055 \text{ litres} = 70.55 \text{ mL}$$

As explained earlier, when all the Cu^{2+} ion will be deposited at cathode, H^+ ions will start going to cathode liberating hydrogen (H_2) gas, *i.e.*

$$H^+ + e^- \rightleftharpoons H \rightleftharpoons H + H \rightarrow H_2$$

However, the anode reaction remains same as previous. Thus in the second (latter) case, amount of H_2 collected at cathode should be calculated.

8 g of O_2 ≡ 1 g of H_2

5.6 litres of O_2 at NTP = 11.2 litres of hydrogen

Quantity of electricity passed after 1st electrolysis,

i.e. Q = i × t = 1.2 × 7 × 60 = 504 coulombs

$$504 \text{ coulombs will liberate} = \frac{5.6\times504}{96500} = 29.24 \text{ mL of } O_2.$$

Similarly, H_2 liberated by 504 coulombs

$$= 11.2\times\frac{504}{96500} = 58.48 \text{ mL}$$

(Twice the volume of O_2 liberated in latter phase
= 2 × 29.24 = 58.48 mL)

Total volume of O_2 liberated = 70.55 + 29.24 = **99.79 mL**

Vol. of H_2 liberated = **58.48 mL**

32. For the given reactions, it is obvious that 22.4 litres of H_2 gas require 2 Faraday electricity.

$\therefore$ 67.2 litres of H_2 will produce = 6 Faraday electricity

$Q = i\times t;\ 6\times96500 = i\times15\times60$

$$i = \frac{6\times96500}{15\times60} = \mathbf{643.3\ ampere}$$

Calculation of amount of Cu deposited by 6 F

Since 1 F deposits $= \frac{63.5}{2} = 31.75$ g of Cu

6 F will deposit $= 31.75 \times 6$ g $=$ **190.50 g**

33. In lead storage battery, the anodic and cathodic reactions during discharge (or operation or working) are as :

(i) Anodic reaction :

$$Pb(s) + SO_4^{2-}(aq) \longrightarrow PbSO_4(s) + 2e^-$$

(ii) Cathodic reaction :

$$PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \longrightarrow PbSO_4(s) + 2H_2O(l)$$

In both the half cell reactions, H_2SO_4 is consumed and hence, conc. of H_2SO_4 decreases during the working (discharging, of the battery. For the withdrawl of 2F = 2 × 96500 C of electric charge, 2 mol of H_2SO_4 are consumed. Density of H_2SO_4 solution (used as electrolyte) falls during working of the cell.

Both reactions get reversed on charging the battery, leading to regeneration of H_2SO_4 as :

Formerly anode but now cathode (recharging)

$$PbSO_4(s) + 2e^- \longrightarrow Pb(s) + SO_4^{2-}(aq)$$

Formerly cathode but now anode :

$$PbSO_4(s) + 2H_2O(l) \rightarrow PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^-$$

Molarity of H_2SO_4 before electrolysis

$$= \frac{39 \times 1.294 \times 1000}{98 \times 100}$$

$= 5.15$ M

Moles of H_2SO_4 before electrolysis

$= 5.15 \times 3.5 = 18.025$

Molarity of H_2SO_4 after electrolysis

$$= \frac{20 \times 1.139 \times 1000}{98 \times 100}$$

$= 2.32$ M

Moles of H_2SO_4 after electrolysis

$= 2.32 \times 3.5 = 8.12$

The overall discharging reaction is :

$$Pb(s) + PbO_2(s) + 2SO_4^{2-} + 4H^+ \longrightarrow 2PbSO_4 + 2H_2O$$

Here, $2SO_4^{2-}$ requires $2e^-$ hence n-factor = 1

i.e. $N_{H_2SO_4} = M_{H_2SO_4}$

Equivalent mass of $H_2SO_4 = 98/1 = 98$

Moles or equivalents of H_2SO_4 used

$= 18.025 - 8.12 = 9.905$

Number of coulomb required $= 9.905 \times 96500$

$i \times t = 955350$ A-s

$= 265.375$ A-h

34. Gold deposited in the first cell = 9.85 g

At. wt. of Gold = 197, Oxidation number of gold = +3

Eq. Wt. of Gold $= \frac{197}{3}$

$W = Zit$

$\because$ Charge required to deposit 1 g eq. of gold = 1F = 96,500 C

$\therefore$ Charge required to deposit 9.85 g of gold or

$$\frac{9.85}{197/3} \text{ g eq. of gold} = \frac{96{,}500 \times 9.85 \times 3}{197} \text{ C}$$

$$= 965 \times 5 \times 3 \text{ C} = 14475 \text{ C}$$

According to Faraday's second law,

$$\frac{\text{Wt. of Cu}}{\text{Eq. wt. of Cu}} = \frac{\text{Wt. of Gold}}{\text{Eq. wt. of Gold}}$$

$$\Rightarrow \text{Wt. of Cu deposited} = \frac{9.85 \times 3}{197} \times \frac{63.5}{2} = \mathbf{4.7625 \text{ g}}$$

$$\text{Current} = \frac{Q}{t} = \frac{14475}{5 \times 3600} \text{ A} = \frac{193}{240} \text{ A} = \mathbf{0.8042 \text{ A}}$$

Topic-2: Nernst Equation, Commercial Cells and Corrosion

1. (b) $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

$$\Delta G = \Delta G^\circ + 2.303\, RT \log_{10} Q;\ Q = \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

$[\Delta G^\circ = -nFE^\circ] = -2 \times F \times 1.1$

Given $[Zn^{2+}] = 10[Cu^{2+}]$

$$\therefore\ \Delta G = -2F(1.1) + 2.303\, RT \log_{10} 10 = 2.303\, RT - 2.2F$$

2. (d) At anode : $H_2(g) \rightleftharpoons 2H^+(aq) + 2e^-$

At cathode : $M^{4+}(aq) + 2e^- \rightleftharpoons M^{2+}(aq)$

Net cell reaction : $H_2(g) + M^{4+}(aq) \rightleftharpoons 2H^+(aq) + M^{2+}(aq)$

$$\text{Now, } E_{cell} = \left(E^\circ_{M^{4+}/M^{2+}} - E^\circ_{H^+/H_2}\right) - \frac{0.059}{n} \cdot \log \frac{[H^+]^2[M^{2+}]}{P_{H_2} \cdot [M^{4+}]}$$

$$\text{or, } 0.092 = (0.151 - 0) - \frac{0.059}{2} \cdot \log \frac{1^2 \times [M^{2+}]}{1 \times [M^{4+}]}$$

$$\therefore\ \frac{[M^{2+}]}{[M^{4+}]} = 10^2 \Rightarrow x = 2$$

3. (d) Here $n = 4$, and $[H^+] = 10^{-pH} = 10^{-3}$

Applying Nernst equation

$$E = E^\circ - \frac{0.059}{n} \log \frac{[Fe^{2+}]^2}{[H^+]^4\, p_{O_2}}$$

$$=1.67-\frac{0.059}{4}\log\frac{(10^{-3})^2}{(10^{-3})^4\times 0.1}$$

$$=1.67-\frac{0.03}{2}\log 10^7=1.67-0.105=1.565\text{ V}$$

4. **(a)** $Fe(s)\longrightarrow Fe^{2+}+2e^-;\quad E^\circ=0.44\text{ V}$
$2H^+ + 2e^- + \frac{1}{2}O_2 \longrightarrow H_2O(l);\quad E^\circ=+1.23\text{ V}$
$Fe(s)+2H^+ + \frac{1}{2}O_2\longrightarrow Fe^{2+}+H_2O;$
$E^\circ_{cell}=0.44+1.23=1.67\text{ V}$
$\therefore\quad \Delta G^\circ=-nFE^\circ_{cell}=-2\times 96500\times 1.67=-322\text{ kJ}$

5. **(b)** Cell reaction : $Zn+Fe^{2+}\longrightarrow Zn^{2+}+Fe$
Using Nernst equation

$$E_{cell}=E^\circ_{cell}-\frac{0.0591}{n}\log\left[\frac{Zn^{2+}}{Fe^{2+}}\right]$$

$$E_{cell}=E^\circ_{cell}-\frac{0.0591}{2}\log\frac{10^{-2}}{10^{-3}}$$

At 298 K, $E=0.2905$

$$E^\circ_{cell}=0.2905+\frac{0.0591}{2}=0.32$$

or $\quad 0.32=\frac{0.0591}{2}\log K_{eq.}\quad$ or $K_{eq}=10^{\frac{0.32}{0.0295}}$.

6. **(c)** In an electrolytic cell, electrons do not flow themselves. It is the migration of ions towards oppositely charged electrodes that indirectly constitutes the flow of electrons from cathode to anode through internal supply.

7. **(a)** MnO_4^- will oxidise Cl^- ion according to the following equation:

$$2MnO_4^- + 16H^+ + 10Cl^- \longrightarrow 2Mn^{2+}+8H_2O+5Cl_2\uparrow$$

The cell corresponding to this reaction is as follows :
$Pt, Cl_2\,(1\text{ atm})\,|\,Cl^-\,||\,MnO_4^-, Mn^{2+}, H^+\,|\,Pt$
$E^\circ_{cell}=1.51-1.40=0.11\text{ V}$
E°_{cell} being +ve, ΔG° will be –ve and hence, the above reaction is feasible. MnO_4^- will not only oxidise Fe^{2+} ion but also Cl^- ion simultaneously. So, the quantitative estimation of aq $Fe(NO_3)_2$ cannot be done by this.

8. **(c)** The salt used to make 'salt–bridge' must be such that the ionic mobility of cation and anion are of comparable order so that they can keep the anode and cathode half cells neutral at all times. KNO_3 is used becasue velocities of K^+ and NO_3^- ions are nearly same.

9. **(b)** For $M^+ + X^- \longrightarrow M+X$, $E^\circ_{cell}=0.44-0.33=0.11\text{ V}$ is positive, hence reaction is spontaneous.

10. **(a)** The given order of reduction potentials is $Z>Y>X$. A spontaneous reaction will have the following characteristics:
(i) Z reduced and Y oxidised,
(ii) Z reduced and X oxidised and
(iii) Y reduced and X oxidised
Hence, Y will oxidise X and not Z.

11. **(c)** We have

Half -cell	**Half-cell reaction**	$\Delta G^\circ=-nFE^\circ$
$Cu^{2+}\,|\,Cu$	$Cu^{2+}+2e^-=Cu$	$\Delta G_1^\circ=-2FE^\circ_{Cu^{2+}|Cu}$
$Cu^{2+}\,|\,Cu^+$	$Cu^{2+}+e^-=Cu^+$	$\Delta G_2^\circ=-FE^\circ_{Cu^{2+}|Cu^+}$
$Cu^+\,|\,Cu$	$Cu^++e^-=Cu$	$\Delta G_3^\circ=-FE^\circ_{Cu^+|Cu}$

From the half-cell reactions, it follows that

$$\Delta G_3^\circ=\Delta G_1^\circ-\Delta G_2^\circ$$

i.e., $-FE^\circ_{Cu^+|Cu}=-2FE^\circ_{Cu^{2+}|Cu}-\left(-FE^\circ_{Cu^{2+}|Cu^+}\right)$

or $E^\circ_{Cu^+|Cu}=2E^\circ_{Cu^{2+}|Cu}-E^\circ_{Cu^{2+}|Cu^+}$
$=2(0.337\text{ V})-0.153\text{ V}=0.521\text{ V}$

12. **(a)** H_2O is more readily reduced at cathode than Na^+. It is also more readily oxidized at anode than SO_4^{2-}. Hence, the electrode reactions are

$$2H_2O+2e^-\longrightarrow H_2\uparrow+2OH^-\ \text{[at cathode]}$$

$$H_2O\longrightarrow \frac{1}{2}O_2\uparrow+2H^++2e^-\ \text{[at anode]}$$

13. **(b)**
(i) In a galvanic cell oxidation occurs at anode and reduction occurs at cathode.
(ii) Oxidation occurs at electrode having higher oxidation potential and it behaves as anode and other electrode acts as cathode.
(iii) $E_{Cell}=E_C-E_A$
(substitute reduction potential at both places).

$$Fe^{2+}+Zn\longrightarrow Zn^{2+}+Fe$$

$\because Zn\longrightarrow Zn^{++}+2e^-$ and $Fe^{2+}+2e^-\longrightarrow Fe$
$\therefore$ Zn is anode and Fe is cathode.
$E_{cell}=E_C-E_A=-0.41-(-0.76)=0.35\text{V}.$

14. **(a)** Water is reduced at the cathode and oxidized at the anode instead of Na^+ and SO_4^{2-}.

Cathode : $2H_2O+2e^-\rightarrow H_2+2OH^-;\ E^\circ=-0.83\text{ V}$

Anode : $H_2O\rightarrow 2H^++\frac{1}{2}O_2+2e^-;\ E^\circ=-1.23\text{ V}$

Note : The standard electrode, reduction potential of Na^+ is less than that of water.

$$Na^++e^-\underset{\text{oxidation}}{\longrightarrow}Na(s)\qquad E^\circ=-2.71\text{ V}$$

The standard electrode, oxidation potential of SO_4^{2-} is less than that of water.

$$2SO_4^{2-}\longrightarrow S_2O_8^{2-}+2e^-\qquad E^\circ=-2.01\text{ V}$$

15. **(c)** Oxidation is loss of electron and in a galvanic cell it occurs at anode. Reduction is gain of electron and in a galvanic cell it occurs at cathode.

Cell representation :

Anode / Anodic electrolyte || Cathodic electrolyte / Cathode

Reaction at Anode : $H_2 \rightarrow 2H^+ + 2e^-$

Reaction at Cathode : $AgCl + e^- \rightarrow Ag + Cl^-$

16. **(c)** The reduction potentials (as given) of the ions are in the order :

$Ag^+ > Hg_2^{2+} > Cu^{2+} > Mg^{2+}$

Mg^{2+} (aq.) will not be reduced as its reduction potential is much lower than that of water (–0.83 V).

Hence, the sequence of deposition of the metals will be Ag, Hg, Cu.

17. **(a)** More negative is the value of reduction potential, higher will be the reducing property, *i.e.,* the power to give up electrons.

18. **(10)**

$$Mg(s) \longrightarrow Mg^{2+}(aq) + 2e^-$$

$$\underline{Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)}$$

$$Mg(s) + Cu^{2+}(aq) \longrightarrow Mg^{2+}(aq) + Cu(s)$$

$$E_{cell} = E^\circ_{cell} - \frac{RT}{nF}\ln x$$

$$E = 2.67 = 2.7 - \frac{RT}{nF}\ln\frac{x}{1}$$

$$0.03 = \frac{300}{2 \times 11500}\ln x$$

$$2.3 = \ln x;\ x = 10$$

19. **(4)** $X \longrightarrow Y;\qquad \Delta G^\circ = -193\ \text{kJ mol}^{-1}$

$$M^+ \longrightarrow M^{3+} + 2e^- \qquad E^\circ = -0.25V$$

Hence ΔG° for oxidation will be

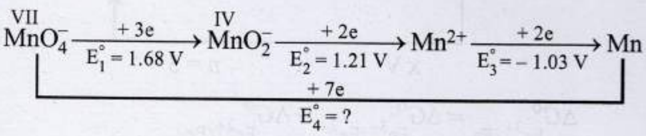
$$\Delta G^\circ = -nFE^\circ$$

$$= -2 \times 96500 \times (-0.25) = 48250\ J = 48.25\ kJ$$

48.25 kJ energy oxidises one mole M^+

$\therefore$ 193 kJ energy oxidises $\frac{193}{48.25}$ mole $M^+ = 4$ mole M^+

20. **(0.77)**



$$\Delta G_4^\circ = G_1^\circ + \Delta G_2^\circ + \Delta G_3^\circ$$

$$\text{or } -n_4FE_4^\circ = n_1FE_1^\circ - n_2FE_2^\circ - n_3FE_3^\circ$$

[Applying Nernst Eq.]

$$\text{or } -7E_4^\circ = -3E_1^\circ - 2E_2^\circ - 2E_3^\circ$$

$$\text{or}\quad E_4^\circ = \frac{(3 \times 1.68) + (2 \times 1.21) - (2 \times 1.03)}{7}V = 0.77\,V$$

21. **(– 11.62)**

$A(s) \mid A^{n+}(aq, 2M) \parallel B^{2n+}(aq, 1M) \mid B(s)$

Reactions

$$\text{Anode}\qquad (A \longrightarrow A^{n+} + ne^-) \times 2$$

$$\underline{\text{Cathode}\qquad B^{2n+} + 2ne^- \longrightarrow B}$$

Overall reaction :

$$2A + B^{2n+} \longrightarrow 2A^{n+} + B$$

$$E = E^\circ - \frac{RT}{2nF}\ln Q$$

$$0 = E^\circ - \frac{RT}{2nF}\ln\frac{[A^{n+}]^2}{[B^{2n+}]}$$

$$E^\circ = \frac{RT}{2nF}\ln\frac{2^2}{1};\ E^\circ = \frac{RT}{2nF}\ln 4$$

$$\text{Now, } \Delta G^\circ = -2nFE^\circ = -\frac{2nFRT}{2nF}\ln 4 = -RT\ln 4$$

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 2\Delta G^\circ - T\Delta S^\circ$ (Given $\Delta H^\circ = 2\Delta G^\circ$)

$$T\Delta S^\circ = \Delta G^\circ$$

$$\Delta S^\circ = \frac{\Delta G^\circ}{T} = \frac{-RT\ln 4}{T} = -R\ln 4 = -R \times 2\ln 2$$

$$= -8.3 \times 2 \times 0.7 = -11.62\ JK^{-1}\ mol^{-1}$$

22. **(0.05)** Daniel cell is : $Zn \mid Zn^{2+} \parallel Cu^{2+} \mid Cu$

Let there be two Daniel cells with their E_{cell} as given below:

$Zn \mid Zn^{2+}(C_1) \parallel Cu^{2+}(C = ?) \mid Cu,$

$E_{cell} = E_1$

$Zn \mid Zn^{2+}(C_2) \parallel Cu^{2+}(C = 0.5\,M) \mid Cu$

$E_{cell} = E_2$ where $E_2 > E_1$

According to question, $E_2 - E_1 = 0.03$ and $C_2 = C_1$

The cell reaction is

$$Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu, Q = \frac{[Zn^{2+}]}{[Cu^{2+}]}.$$

$$\text{Thus, } E_1 = E^o_{cell} - \frac{0.06}{2}\log\frac{C_1}{C};$$

$$\text{and } E_2 = E^o_{cell} - \frac{0.06}{2}\log\frac{C_2}{0.5};$$

Since, same $ZnSO_4$ is used in both cells $C_1 = C_2$

$$\text{So, } E_2 - E_1 = \frac{0.06}{2}\left[\log\frac{C_1}{C} \times \frac{0.5}{C_1}\right]$$

$$\Rightarrow 0.03 = \frac{0.06}{2}\log\frac{0.5}{C} \Rightarrow \log\frac{0.5}{C} = 1 \text{ or } C = \mathbf{0.05\,M}$$

23. **(–0.22)** At pH = 14; $[H^+] = 1 \times 10^{-14}$ M; $[OH^-] = 10^0 = 1M$ $(\because [H^+][OH^-] = 1 \times 10^{-14})$

$\therefore$ $Cu(OH)_2$ ionises as follows:

$$Cu(OH)_2 \rightleftharpoons Cu^{2+} + 2OH^-$$

$\therefore K_{sp}$ of $Cu(OH)_2 = [Cu^{2+}][OH^-]^2$

$$1.0 \times 10^{-19} = [Cu^{2+}][1]^2 ; [Cu^{2+}] = 1.0 \times 10^{-19}\,M$$

The standard reduction potential of Cu^{2+}/Cu is represented in the form of following equation:

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$$

On applying Nernst equation

$$E = E^{o} - \frac{0.0591}{n} \log \frac{1}{[Cu^{2+}]}$$

$$= +0.34 - \frac{0.0591}{2} \log \frac{1}{1 \times 10^{-19}}$$

$$= \left[0.34 - \frac{0.0591}{2} \times 19\right] = 0.34 - 0.56 = \mathbf{-0.22V}$$

24. **(0.792)**

$$\begin{array}{lcccc} & 2Hg + 2Fe^{3+} & \longrightarrow & Hg_2^{2+} & + \; 2Fe^{2+} \\ \text{Initial conc.} & 1.0 \times 10^{-3} & & 0 & 0 \\ \text{Eqilb. conc.} & 0.05 \times 10^{-3} & & \frac{0.95 \times 10^{-3}}{2} & 0.95 \times 10^{-3} \end{array}$$

$$E = E^{o}_{Fe^{3+}/Fe^{2+}} - E^{o}_{Hg_2^{2+}/Hg} - \frac{0.059}{n} \log \frac{[Fe^{2+}]^2[Hg_2^{2+}]}{[Fe^{3+}]^2}$$

At equilibrium, $E = 0$

$$\Rightarrow 0 = 0.77 - E^{o}_{Hg_2^{2+}/Hg} - \frac{0.059}{2} \log \frac{(0.95 \times 10^{-3})^2 (0.475 \times 10^{-3})}{(0.05 \times 10^{-3})^2}$$

On usual calculations, $E^{o}_{Hg_2^{2+}/Hg} = \mathbf{0.792V}$

25. **negative, greater;** Among the various metals, since sodium has the minimum reduction potential, it must be strongest reducing agent. In general, more the reduction potential lesser is its reducing action.

26. **False :** When the temperature is 273 K, the value of the factor will come out as 0.0541 instead of 0.0591. The value 0.0591 comes out at 298 K and not at 273 K.

27. **(b, c, d)**

(a) $M(s) + 2H^+(aq) \longrightarrow H_2(g) + M^{2+}(aq)$

No. of moles of exchanged e^-, $n = 2$

$$\Delta S = nF \frac{dE_{cell}}{dT} = 2F\left(\frac{R}{F}\right) = 2R$$

(b) $Pt(s) \mid H_2(g), 1\text{ bar} \mid H^+(aq, 0.01\,M) \| H^+(aq, 0.1\,M) \mid H_2(g, 1\text{ bar}) \mid Pt(s)$

$$E_{cell} = \frac{2.303RT}{nF} \log \frac{0.01}{0.1}$$

$$\Rightarrow E_{cell} = \frac{2.303RT}{F} > 0 \Rightarrow \Delta G < 0$$

For concentration cell, $\Delta H = 0$

$\Delta G = \Delta H - T\Delta S \Rightarrow \Delta S > 0$

Hence, it is an entropy driven process.

(c) Racemization of an optically active compound is a spontaneous process, i.e., $\Delta G < 0$.

As $\Delta H = 0 \Rightarrow \Delta S > 0$

(d) $[Ni(H_2O)_6]^{2+} + 3\,en \longrightarrow \underset{\text{more stable}}{[Ni(en)_3]^{2+}} + 6H_2O$

The no. of molecules in the product side is increasing hence, $\Delta S > 0$.

28. **(a, b, c)**

$$X(s) \rightarrow X^{+2}(0.001M) + 2e^-\ (\text{anode})$$

$$Y^{+2}(0.1M) + 2e^- \rightarrow Y(s)(\text{cathode})$$

$$E_{cell} = E^{o}_{cell} - \frac{0.06}{2} \log \frac{X^{+2}}{Y^{+2}}$$

$E_{cell} = E^{o}_{cell} + 0.06$

(a) Cd (X) and Ni (Y) $E^{o}_{cell} = +0.4 - 0.24 ; E_{cell} = 0.22$

(b) Cd (X) and Fe (Y) $E^{o}_{cell} = -0.04 ; E_{cell} = 0.02$

(c) Ni (X) and Pb (Y) $E^{o}_{cell} = 0.11 ; E_{cell} = 0.17$

(d) Ni (X) and Fe (Y) $E^{o}_{cell} = -0.2 ; E_{cell} = -0.14$

Since in (a) (b) (c), E_{cell} is positive, hence answer is (a) (b) (c).

29. **(a)** Salt bridge is introduced to keep the solutions of two electrodes separate, so that the ions in electrodes do not mix freely with each other. Salt bridge maintains the diffusion of ions from one electrode to another.

30. **(a, b, d)**

The species having less reduction potential with respect to NO_3^- ($E^\circ = +0.96$ V) will be oxidised by NO_3^-. These species are V, Fe and Hg.

31. **(a)** More negative or lower is the reduction potential, more is the reducing property. Thus, the reducing power of the corresponding metal will follow the reverse order, *i.e.* $Y > Z > X$.

32. **(d)** (P)

$$\begin{tikzcd} Fe^{3+} \arrow[r, "+0.77V", "n=1"'] \arrow[rr, bend right, "xV \qquad n=3"'] & Fe^{2+} \arrow[r, "-0.44V", "n=2"'] & Fe \end{tikzcd}$$

$$\Delta G^{o}_{Fe^{3+}/Fe} = \Delta G^{o}_{Fe^{3+}/Fe^{2+}} + \Delta G^{o}_{Fe^{2+}/Fe}$$

$$\Rightarrow -3 \times FE^{o}_{(Fe^{+3}/Fe)} = -1 \times FE^{o}_{(Fe^{+3}/Fe^{+2})} + \left(-2 \times FE^{o}_{Fe^{+2}/Fe}\right)$$

$$\Rightarrow 3 \times x = 1 \times 0.77 + 2 \times (-0.44)$$

$$\Rightarrow \quad x = -\frac{0.11}{3}\text{V} \simeq -0.04\,\text{V}.$$

(Q)

$$\begin{array}{rll} 2\text{H}_2\text{O} \longrightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^- & & E° = -1.23\,\text{V} \\ 4\text{e} + \text{O}_2 + 2\text{H}_2\text{O} \longrightarrow 4\text{OH}^- & & E° = +0.40\,\text{V} \\ \hline 4\text{H}_2\text{O} \longrightarrow 4\text{H}^+ + 4\text{OH}^- & & E° = -0.83\,\text{V} \end{array}$$

(R)

$$\begin{array}{rl} \text{Cu}^{2+} + 2\text{e} \longrightarrow \text{Cu} & E° = +0.34\,\text{V} \\ 2\text{Cu} \longrightarrow 2\text{Cu}^+ + 2\text{e} & E° = -0.52\,\text{V} \\ \hline \text{Cu}^{2+} + \text{Cu} \longrightarrow 2\text{Cu}^+ & E° = -0.18\,\text{V} \end{array}$$

(S)

$$\begin{tikzcd} \text{Cr}^{3+} \arrow[r, "x", "n=1"'] \arrow[rr, bend right, "{-0.74\text{V}, \quad n=3}"'] & \text{Cr}^{2+} \arrow[r, "-0.91\text{V}", "n=2"'] & \text{Cr} \end{tikzcd}$$

$$x \times 1 + 2 \times (-0.91) = 3 \times (-0.74)$$
$$x - 1.82 = -2.22 \Rightarrow x = -0.4\text{V}$$

33. (d) **At anode :** $M(\text{s}) + 2X^-(\text{aq}) \longrightarrow MX_2(\text{aq}) + 2\text{e}^-$

At cathode : $M^{+2}(\text{aq}) + 2\text{e}^- \longrightarrow M(\text{s})$

Thus, here $n = 2$

$$\Delta G = -nFE_{\text{cell}}$$
$$= -2 \times 96500 \times 0.059 \times 10^{-3}\,\text{kJ/mole} = -11.4\,\text{kJ/ mole}$$

34. (b) $M(\text{s}) + M^+(\text{aq})1\text{M} \longrightarrow M^+(\text{aq})(.05\text{M}) + M(\text{s})$

According to Nernst equation,

$$E_{\text{cell}} = 0 - \frac{2.303RT}{F}\log\frac{M^+_{(.05\text{M})}}{M^+_{(1\text{M})}}$$

$$= 0 - \frac{2.303RT}{F}\log(5 \times 10^{-2}) = +\text{ve}$$

Hence, $|E_{cell}| = E_{cell} = 0.070$ V and $\Delta G < 0$ for the feasibility of the reaction.

For concentration cell, $E^\circ_{\text{cell}} = 0$

35. (c) From above equation $\frac{-2.303\text{RT}}{F}\log(5 \times 10^{-2}) = 0.07$

$$\Rightarrow \frac{2.303\text{RT}}{F} \times 1.3 = 0.07 \Rightarrow \frac{2.303\text{RT}}{F} = 0.0538$$

$$\text{So, } E_{cell} = E^\circ_{cell} - \frac{0.0538}{1}\log 0.0025$$

$$= 0 - \frac{0.0538}{1}\log 0.0025 \approx 0.13988\text{V} \approx 140\,\text{mV}$$

36. (c) $2\text{I}^- + \text{Cl}_2 \longrightarrow \text{I}_2 + 2\text{Cl}^-$

$$E° = E^\circ_{\text{I}^-/\text{I}_2} + E^\circ_{\text{Cl}_2/\text{Cl}^-} = -0.54 + 1.36;\ E° = 0.82\text{V}$$

$E°$ is positive hence, iodide ion is oxidized by chlorine.

37. (d) $4\text{Mn}^{3+} + 2\text{H}_2\text{O} \longrightarrow 4\text{Mn}^{2+} + \text{O}_2 + 4\text{H}^+$

$$E^\circ_{\text{Mn}^{3+}/\text{Mn}^{2+}} + E^\circ_{\text{H}_2\text{O}/\text{O}_2} = 1.50 + (-1.23) = 0.27\,\text{V}$$

Reaction is feasible. [$\therefore E°$ is positive]

38. (a) The precipitate formed in this reaction is of

$$\overset{\text{III}}{\text{Fe}_4}[\overset{\text{II}}{\text{Fe}}(\text{CN})_6]_3.$$

39. (d) In the given reaction,

Ag^+ ions are reduce to Ag and Glucose is oxidised to gluconic acid as per the given reactions,

$$\text{Ag}^+ + \text{e}^- \longrightarrow \text{Ag};\ E^\circ_{\text{red}} = +0.800\,\text{V} \text{ and}$$

$$\text{C}_6\text{H}_{12}\text{O}_6 + \text{H}_2\text{O} \longrightarrow \underset{\text{Gluconic acid}}{\text{C}_6\text{H}_{12}\text{O}_7} + 2\text{H}^+ + 2\text{e}^-;$$

$$E^\circ_{\text{ox}} = -0.05\text{V}$$

Hence, $E^\circ_{\text{cell}} = 0.8 - 0.05 = 0.75\,\text{V}$

$$\Delta G^\circ_{\text{cell}} = -nFE = -2F \times 0.75 = -RT\ln K$$

$$\Rightarrow \ln K = \frac{2\text{F}}{\text{RT}}(0.75) = 2 \times 38.92 \times 0.75 = 58.38$$

40. (a) For the reaction,

$$\text{C}_6\text{H}_{12}\text{O}_6 + \text{H}_2\text{O} \longrightarrow \underset{\text{Gluconic acid}}{\text{C}_6\text{H}_{12}\text{O}_7} + 2\text{H}^+ + 2\text{e}^-$$

$$E = E° - \frac{0.0591}{n}\log\frac{[\text{P}]}{[\text{R}]} = E° - \frac{0.0591}{2}\log[\text{H}^+]^2$$

$$E - E° = -\frac{0.0591}{2} \times 2(-\text{pH}) = 0.0591 \times 11 = 0.65$$

So, $E_{\text{oxidation}}$ increases over $E^\circ_{\text{oxidation}}$ by 0.65 V.

41. (b) During Tollen's test, oxidation of silver ion requires an alkaline medium. Under these conditions it forms insoluble silver oxide, hence to dissolve this oxide a complexing agent, ammonia is added, which brings silver ion as diamminosilver (I) ion, $[\text{Ag(NH}_3)_2]^+$. It is a soluble complex.

42. (a) From the given details, the reactions can be written as:

$$\begin{array}{ll} \text{At anode:} & \text{Ag(s)} + \text{Cl}^-(\text{aq}) \longrightarrow \text{AgCl(s)} + \text{e}^- \\ \text{At cathode:} & \text{Ag}^+(\text{aq}) + \text{e}^- \longrightarrow \text{Ag(s)} \\ \hline \text{Complete reaction} & \text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \longrightarrow \text{AgCl(s)} \end{array}$$

Hence, cell representation is

$$\text{Ag(s)}\,|\,\text{AgCl(s)}\,|\,\text{Cl}^-(\text{aq})\,||\,\text{Ag}^+(\text{aq})\,|\,\text{Ag(s)}$$

$$\Delta G° = \Delta G^\circ_f(\text{AgCl}) - [\Delta G^\circ_f(\text{Ag}^+) + \Delta G^\circ_f(\text{Cl}^-)]$$
$$= -109 - (-129 + 77) = -57\,\text{kJ/mol} = -57000\,\text{J/mol}$$

We know that, $\Delta G° = -nFE^\circ_{\text{cell}}$

$$-57000 = -1 \times 96500 \times E^\circ_{\text{cell}}$$

($\because n$ = electron transferred = 1)

$$E^\circ_{\text{cell}} = \frac{57000}{96500} = \mathbf{0.59\ volts}$$

$$\text{Again } E^\circ_{\text{cell}} = \frac{0.0591}{n}\log K_c$$

$$\text{or } E^\circ_{\text{cell}} = \frac{0.0591}{n}\log\frac{\text{AgCl}}{[\text{Ag}^+][\text{Cl}^-]}$$

$$E^{\circ}_{\text{cell}} = \frac{0.0591}{1}\log\left(\frac{1}{K_{sp}}\right)$$

$$\text{or } 0.59 = -0.059 \log K_{sp}$$

$$\text{or } \log K_{sp} = -10 \Rightarrow K_{sp} = \mathbf{10^{-10}}$$

(b) When Zn is added to 100 mL of saturated AgCl solution.

$$2\,Ag^+ + Zn(s) \rightleftharpoons 2Ag(s) + Zn^{2+}$$

$$Ag^+ + e^- \rightleftharpoons Ag;\ E^{\circ} = 0.80\,V$$

$$Zn^{2+} + 2\,e^- \rightleftharpoons Zn;\ E^{\circ} = -0.76\,V$$

$$E^{\circ}_{\text{cell}} = E^{\circ}_{Ag^+|Ag(s)} - E^{\circ}_{Zn^{2+}|Zn(s)}$$
$$= 0.80 - (-0.76) = 1.56\,V$$

$$E^{\circ}_{\text{cell}} = \frac{0.059}{n}\log_{10}\frac{[Zn^{2+}]}{[Ag^+]^2}$$

$$\Rightarrow 1.56 = \frac{0.059}{2}\log_{10}\frac{[Zn^{2+}]}{[Ag^+]^2}$$

$$\Rightarrow \log_{10}\frac{[Zn^{2+}]}{[Ag^+]^2} = \mathbf{52.9}$$

As the value of equilibrium constant is very high so the reaction moves in forward direction completely.

$$[Ag^+] \text{ from (a)} = \sqrt{10^{-10}} = 10^{-5}$$
$$[(\because K_{sp} = 10^{-10} = [Ag^+][Cl^-]]$$

$$\therefore Ag^+ \text{ in } 100\,\text{mL of solution} = \frac{10^{-5}\times 100}{1000} = \mathbf{10^{-6}\ mol.}$$

43. The required reaction can be obtained in the following way.

$$Cu^{2+} + e^- \longrightarrow Cu^+ \quad \Delta G^{\circ} = -0.15\,F$$
$$In^{2+} + e^- \longrightarrow In^+, \quad \Delta G^{\circ} = +0.40\,F$$
$$In^+ \longrightarrow In^{3+} + 2e^-, \quad \Delta G^{\circ} = 0.84\,F$$

On adding, $Cu^{2+} + In^{2+} \longrightarrow In^{3+} + Cu^+,\ E^{\circ} = -0.59\,F$

Now we know that $-n\,FE^{\circ} = -0.59\,F$

or $-E^{\circ}_{\text{cell}} = -0.59\text{V}$ or $E^{\circ}_{\text{cell}} = 0.59\text{V}$

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0591}{n}\log K_c\,;$$

$$E_{\text{cell}} = 0,\ 0.59 = \frac{0.0591}{1}\log K_c$$

$$\log K_c = \frac{0.59}{0.0591} = 10\ ; \quad K_c = \mathbf{10^{10}}$$

44. (*i*) The half cell reactions are

At anode $\quad \frac{1}{2}H_2(g) \longrightarrow H^+(aq) + e^-$

At cathode $\quad AgCl(s) + e^- \longrightarrow Ag(s) + Cl^-(aq)$

The cell reaction $\frac{1}{2}H_2(g) + AgCl(s)$

$$\rightleftharpoons H^+(aq) + Ag(s) + Cl^-(aq)$$

(*ii*) We know that $\Delta S^{\circ} = nF\dfrac{dE^{\circ}}{dT}$

$n \rightarrow$ No. of transferred electrons = 1

$F \rightarrow$ faraday number = 96500 coulombs

$dE^{\circ} \rightarrow$ Difference of electrode potential at two different temperatures $= (0.21 - 0.23) = -0.02\text{V}$

$dT \rightarrow$ Difference of two temperatures $= (35°C - 15°C) = 20°C$

$$\therefore \Delta S^{\circ} = 1 \times 96500 \times \frac{-0.02}{20} = -96.5\,J/K\,mole\,;$$

$$\therefore E^{\circ}_{15} = 0.23V\,;\ \Delta G^{\circ} = -nE^{\circ}F$$

so $\Delta G^{\circ}_{15} = -1 \times 0.23 \times 96500\,J = \mathbf{-22195\ Jmole}$

$$\Delta H^{\circ} = \Delta G^{\circ} - T\Delta S^{\circ} = -22195 - 288 \times (-96.5)$$
$$= \mathbf{-49987\ J/mole.}$$

(*iii*) $E^{\circ}_{.25°C}$ of cell

$$= E^{\circ}_{15} - \frac{dE}{dT}\times\Delta T = \left(0.23 - \frac{0.02}{20}\times 10\right)V = 0.22V$$

The corresponding cell is represented as :

$$Ag_{(s)}\,|\,Ag^+_{(aq)}\,\|\,Cl^-_{(aq)}(AgCl_{(s)})\,|\,Ag_{(s)}$$

In form of oxidised electrode potential

$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{anode}} - E^{\circ}_{\text{Cathode}} = E^{\circ}_{Ag/Ag^+} - E^{\circ}_{Ag/AgCl/Cl^-}$$
$$= -0.80 - (0.22) = 0.58V$$

$$E^{\circ}_{\text{cell}} = \frac{0.0591}{n}\log_{10} K_{eq}$$

$$AgCl_{(s)} \rightleftharpoons Ag^+ + Cl^-$$

$$E^{\circ}_{\text{cell}} = \frac{0.0591}{n}\log_{10}[Ag^+][Cl^-] = \frac{0.0591}{n}\log_{10} K_{sp}$$

$$\text{Therefore } -0.58 = \frac{0.0591}{1}\log_{10} K_{sp}$$

or $\log_{10}K_{sp} = -9.8139 = \overline{10}.1861\,;\ K_{sp} = 1.54 \times 10^{-10}$

K_{sp} of AgCl $= 1.54 \times 10^{-10}\,(\text{mole Litre}^{-1})^2$

Solubility of AgCl

$$= \sqrt{K_{sp}} = \sqrt{1.54\times10^{-10}} = \mathbf{1.24\times10^{-5}\ mole/L}$$

45. Given, $E^{\circ}_{Ce^{4+}/Ce^{3+}} = 1.61V\,;\ E^{\circ}_{Fe^{3+}/Fe^{2+}} = 0.77V$

Thus for E°_{cell} to be positive, following reaction should occur

$$Ce^{4+} + Fe^{2+} \longrightarrow Fe^{3+} + Ce^{3+}$$

Hence, Ce^{4+}/Ce^{3+} electrode will act as cathode and Fe^{3+}/Fe^{2+} electrode will act as anode.

Therefore, current will flow from Ce electrode to Fe electrode. Current will **decrease** with time.

46. Note that the given cell will not work as electrochemical cell since ${E^\circ}_{OP_{Cu}} > {E^\circ}_{OP_{Ag+}}$

The equation for electro-chemical cells will be:

$Cu \rightarrow Cu^{2+} + 2e^-$

$2Ag^+ + 2e^- \rightarrow 2Ag$

Thus, e.m.f. of cell $Cu \mid Cu^{2+} \parallel Ag^+ \mid Ag$ will be

$$E_{cell} = {E^\circ}_{OP_{Cu}} + {E^\circ}_{RPAg} + \frac{0.059}{2}\log\frac{[Ag^+]^2}{[Cu^{2+}]}$$

$\because [Ag^+] = 1M$ and $[Cu^{2+}] = 1M$

$\therefore E_{cell} = {E^\circ}_{OP_{Cu}} + {E^\circ}_{RP_{Ag}}$

$$\left({E^\circ}_{cell} = {E^\circ}_{OP_{Cu}} + {E^\circ}_{RP_{Ag}}\right) \Rightarrow E_{cell} = {E^\circ}_{cell}$$

After the passage of 9.65 ampere for 1 hr *i.e.* $9.65 \times 60 \times 60$ Coulomb charge, during which the cell reactions are reversed, the Ag metal passes in solution state and Cu^{2+} ions are discharged. The reactions during the passage of current are:

$2Ag \rightarrow 2Ag^+ + 2e^-$ and $Cu^{2+} + 2e^- \rightarrow Cu$

$$\text{Thus, } Ag^+ \text{ formed} = \frac{9.65 \times 60 \times 60}{96500} = 0.36 \text{ eq.} = 0.36 \text{ mole}$$

$$Cu^{2+} \text{ discharged} = \frac{9.65 \times 60 \times 60}{96500} = 0.36 \text{ eq.} = 0.18 \text{ mole}$$

Thus, $[Ag^+]$ left $= 1 + 0.36 = 1.36$ mole

$[Cu^{2+}]$ left $= 1 - 0.18 = 0.82$ mole.

Now e.m.f. can be given as:

$$E_{cell} = {E^\circ}_{cell} + \frac{0.059}{2}\log\frac{(1.36)^2}{0.82} = {E^\circ}_{cell} + 0.010\text{ V}$$

Thus, E_{cell} increases by **0.010 V.**

47. The cell reaction can be written as:

$$Ag \mid Ag^+(Ag_2CrO_4 Sat.) \parallel Ag^+(0.1M) \mid Ag;\ E = 0.164\text{ V}$$

At cathode : $Ag^+_{cathode} + e^- \longrightarrow Ag$

At anode : $Ag \longrightarrow {Ag^+}_{anode} + e^-$

Net reaction : ${Ag^+}_{cathode} \longrightarrow {Ag^+}_{anode}$; $E = 0.164$ V

Thus here, $n = 1, E = 0.164$ V, $[Ag^+]_{cathode} = 0.1$ M

Let the solubility of Ag_2CrO_4 be S M

Since, Ag_2CrO_4 gives $2Ag^+$.

$\therefore$ Here, concentration of $[Ag^+]_{anode} = 2S$ M

$$E = E^\circ - \frac{0.059}{n}\log\frac{[Product]}{[Reactant]}$$

(for a concentration cell, $E^\circ = 0$)

$$\therefore 0.164 = -\frac{0.059}{1}\log\frac{[Ag^+]_{anode}}{[Ag^+]_{cathode}}$$

$$0.164 = -\frac{0.059}{1}\log\frac{2S}{0.1}$$

$$\text{or } 0.164 = \frac{0.059}{1}\log\frac{0.1}{2S} \quad \therefore 2S = 1.697 \times 10^{-4}$$

Hence, $S = 0.8485 \times 10^{-4}$ M

For Ag_2CrO_4; $Ag_2CrO_4 \rightleftharpoons 2Ag^+ + CrO_4^{2-}$

$K_{sp} = (2S)^2(S) = 4S^3$

$\therefore K_{sp} = 4 \times (0.8485 \times 10^{-4})^3 = \mathbf{2.44 \times 10^{-12}}$

48. For the change $2Fe^{3+} + 3I^- \rightleftharpoons 2Fe^{2+} + I_3^-$,

$${E^o}_{cell} = E^o_{RP_{Fe^{3+}/Fe^{2+}}} + {E^o}_{OP_{I^-/I_3^-}} = 0.77 - 0.54 = 0.23\text{ V}$$

$$E_{cell} = E^o_{cell} - \frac{0.059}{2}\log K_c$$

At equilibrium, $E_{cell} = 0$ (Using Nernst equation)

$$\text{Thus, } 0.23 = \frac{0.059}{2}\log K_c \quad \therefore K_C = \mathbf{6.26 \times 10^7}$$

49. $Fe^{2+}(aq) \longrightarrow Fe^{3+}(aq) + e^-$; $E^\circ = 0.68$V

$Ce^{4+}(aq) + e^- \longrightarrow Ce^{3+}(aq)$; $E^\circ = 1.44$V

${E^\circ}_{cell} = 1.44 - 0.68 = +0.76$ V

At equilibrium, $E_{cell} = 0$

$${E^\circ}_{cell} = \frac{0.0591}{n}\log_{10} K_c;\ 0.76 = \frac{0.0591}{1}\log_{10} K_c$$

$$\text{or } \log_{10} K_c = \frac{0.76}{0.0591} = 12.859 \quad \therefore \mathbf{K_c = 7.6 \times 10^{12}}$$

50. The thin protective layer of oxides of aluminium is formed which protects the metal from further attack of water and air and make it stable.

51. (*i*) Given $E^\circ_{Ni_2O_3/NiO} = +0.40$ V; $E^\circ_{FeO/Fe} = -0.87$ V

$E^\circ_{NiO/Ni_2O_3} = -0.40$ V; $E^\circ_{Fe/FeO} = +0.87$V

Since $E^o_{ox.}$ for Fe/FeO > $E^o_{ox.}$ for NiO/Ni_2O_3.

Redox changes can be written as

At anode : $Fe(s) + 2OH^- \rightarrow FeO(s) + H_2O(l) + 2e^-$

At cathode : $Ni_2O_3(s) + H_2O(l) + 2e^- \rightarrow 2NiO(s) + 2OH^-$

Cell reaction : $Fe(s) + Ni_2O_3(s) \rightarrow FeO(s) + 2NiO(s)$

(*ii*) $E_{cell} = E^o_{OP\ Fe/FeO} + E^o_{RP\ Ni_2O_3/NiO}$

$= 0.87 + 0.40 = \mathbf{1.27\ V}$

It is independent of conc. of KOH.

(*iii*) Electrical energy $= nFE_{cell} = 2 \times 96500 \text{ J V}^{-1} \times 1.27$ V

$= \mathbf{2.45 \times 10^5\ J}$

52. E° = Standard reduction potential of the Ag^+/Ag electrode $= 0.799$ V

$AgI(s) \rightleftharpoons Ag^+ + I^-$

$K_{sp} = [Ag^+][I^-] = 8.7 \times 10^{-17}$ (given)

If 'S' is the solubility of AgI, then $K_{sp} = S^2$

$\therefore S = \sqrt{K_{sp}} = \sqrt{8.7 \times 10^{-17}} = 9.327 \times 10^{-9} \text{ mol L}^{-1}$

$\therefore [Ag^+] = [I^-] = 9.327 \times 10^{-9}$ M

Reaction : $Ag^+ + e^- \longrightarrow Ag$

$$\therefore E = E^{\circ} - \frac{0.059}{n} \log \frac{[Ag]}{[Ag^+]}$$

$$= 0.799\text{ V} - \frac{0.059}{1} \log \frac{1}{9.327 \times 10^{-9}}\text{ V}$$

[∵ Activity of the electrode material in pure solid state is taken as one]

$$= 0.799 - 0.059 \log 0.1072 \times 10^{9}\text{ V}$$

$$= 0.799 - 0.474 = \mathbf{0.325\ V}$$

Again,

L.H.S. electrode reaction :

$Ag \rightarrow Ag^+ + e^-$

R.H.S. electrode reaction : $AgI(s) + e^- \rightarrow Ag + I^-$

Cell reaction : $AgI(s) \rightarrow Ag^+ + I^-$

K = Equilibrium constant $= [Ag^+][I^-] = 8.7 \times 10^{-17}$

The standard cell emf E° and the equilibrium constant K are related by the expression:

$$E^{o}_{cell} = \frac{0.059}{n} \log K \text{ at } 298\text{ K}, \quad \text{Here, } n = 1, K = 8.7 \times 10^{-17}$$

$$E^{o}_{cell} = 0.059 \log 8.7 \times 10^{-17} = 0.059\,[0.9395 - 17] = -0.948\text{ V}$$

But $E^{o}_{cell} = E^{o}_{\text{R.H.S.}} - E^{o}_{\text{L.H.S.}}$

$$\therefore E^{o}_{\text{R.H.S.}} = E^{o}_{cell} + E^{o}_{\text{L.H.S.}} = -0.948 + 0.799 = \mathbf{-0.149\ V}$$

53. For the half-cell reaction

$$NO_3^-(aq) + 2H^+(aq) + e^- \longrightarrow NO_2(g) + H_2O(l)$$

The Nernst equation is $E = E^{\circ} - \frac{0.059}{n} \log \frac{[\text{Products}]}{[\text{Reactants}]}$

Substituting the values in case of (i)

$$E = 0.78 - \frac{0.059}{1} \log \frac{1}{(8)^2} = 0.78 + 0.059 \log 64 = \mathbf{0.887\ V}$$

Substituting the value in the Nernst equation in case (ii)

$$E = 0.78 - \frac{0.059}{1} \log \frac{1}{(10^{-7})^2} = 0.78 - 0.059 \log 10^{-14}$$

$$= 0.78 - (0.059) \times (14) = \mathbf{-0.046\ V}$$

54. $2Cl^-(aq) + 2H_2O = 2OH^-(aq) + H_2(g) + Cl_2(g)$

Reaction at anode : $2Cl^- \rightarrow Cl_2 + 2e^-$

Reaction at cathode : $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

$$i = \frac{62}{100} \times 25 = 15.4 \text{ amperes}$$

Weight of Cl_2 deposited = 1 kg or 1000 g

We know that $\frac{W}{E} = \frac{Q}{F} = \frac{it}{F};\ \frac{1000}{35.5} = \frac{15.4 \times t}{96500}$

t = 175300 sec. or **48.69 hours**

No. of moles of Cl_2 thus produced $= \frac{1000}{71} = 14.08$

Amount of OH^- released in the electrolysis $= 2 \times 14.08$ moles $= 28.16$ moles

$$\therefore \text{Molarity with respect to } OH^- = \frac{28.16\text{ mol}}{20\text{ L}} = \mathbf{1.408\ M}$$

55. $Ag\,|\,AgCl(s), KCl(0.2M)\,\|\,KBr(0.001M), AgBr(s)\,|\,Ag$

Anode Cathode

$K_{sp}(AgCl) = 2.8 \times 10^{-10}$ $K_{sp}(AgBr) = 3.3 \times 10^{-13}$

At anode, ${}_1Ag \rightarrow {}_1Ag^+ + e^-$

At cathode, ${}_2Ag^+ + e^- \rightarrow {}_2Ag$

$\therefore$ Cell reaction ${}_1Ag + {}_2Ag^+ \rightarrow {}_2Ag + {}_1Ag^+$

The subscripts 1 and 2 on Ag denote the species concerned with anode and cathode respectively.

Applying Nernst equation

$$E = E^{\circ} - \frac{0.059}{n} \log \left[\frac{\text{Products}}{\text{Reactants}}\right]$$

$$= 0 - \frac{0.059}{1} \log \left[\frac{{}_2Ag \times {}_1Ag^+}{{}_1Ag \times {}_2Ag^+}\right]$$

$[{}_1Ag] = [{}_2Ag] = 1$ (∵ these are in solid state)

$K_{sp}(AgCl) = 2.8 \times 10^{-10}$ or $[{}_1Ag^+][Cl^-] = 2.8 \times 10^{-10}$

$$[{}_1Ag^+] = \frac{2.8 \times 10^{-10}}{0.2} = 14 \times 10^{-10}$$

(∵ $[Cl^-] = 0.2$)

$K_{sp}(AgBr) = 3.3 \times 10^{-13}$ or $[{}_2Ag^+][Br^-] = 3.3 \times 10^{-13}$

$$[{}_2Ag^+] = \frac{3.3 \times 10^{-13}}{0.001} = 3.3 \times 10^{-10} \quad (\because [Br^-] = 0.001)$$

$$\therefore E = -\frac{0.059}{1} \log \left[\frac{14 \times 10^{-10}}{3.3 \times 10^{-10}}\right]$$

$$= -0.059 \log \left[\frac{14}{3.3}\right] = -0.059 \times 0.6276 = \mathbf{-0.037\ V}$$

Since, emf is negative this shows that the reaction is non-spontaneous.

For the reaction to be spontaneous, its emf should be positive *i.e.* **E = 0.037 V** and its polarities should be reversed *i.e.* anode should be made cathode and *vice-versa*.

So, the galvanic cell is : $Ag\,|\,AgBr(s), KBr\,\|\,AgCl(s), KCl\,|\,Ag$

In other words, $Ag\,|\,AgBr$ acts as anode and $AgCl\,|\,Ag$ acts as cathode.

56. The following chemical cell sets up :

$Zn\,|\,Zn^{2+}\,\|\,Ni^{2+}\,|\,Ni$

The net cell reaction is : $Zn + Ni^{2+} \rightleftharpoons Zn^{2+} + Ni$

The e.m.f. is given by

$$E_{\text{cell}} = E^{o}_{Ni^{2+}/Ni} - E^{o}_{Zn^{2+}/Zn} - \frac{0.059}{2} \log \frac{[Zn^{2+}]}{[Ni^{2+}]}$$

$$= -0.24 - (-0.75) - 0.0295 \log \frac{[Zn^{2+}]}{[Ni^{2+}]}$$

$$= 0.51 - 0.0295 \log \frac{[Zn^{2+}]}{[Ni^{2+}]}$$

At equilibrium $E_{\text{cell}} = 0$

Let x mol L^{-1} be the concentration of Ni^{2+} at equilibrium.

Then $[Zn^{2+}] = 1 - x$ [∵ 1 mole of Ni^{2+} gives 1 mole of Zn^{2+}]

$$\therefore 0.0295 \log \frac{1-x}{x} = 0.51$$

$$\text{or } \log \frac{1-x}{x} = \frac{0.51}{0.0295} = 17.29 \text{ or } \frac{1-x}{x} = 1.95 \times 10^{17}$$

$$\text{or } x = \frac{1}{1.95 \times 10^{17}} = \mathbf{5.128 \times 10^{-18}\ mol^{-1}}$$

57. $E^{\circ}_{Cu^{2+}/Cu} = 0.337$ and $E^{\circ}_{Ag^{+}/Ag} = 0.799$ V

$$E^{\circ}_{Ag^{+}/Ag} + E^{\circ}_{Cu/Cu^{2+}} = 0.799 - 0.337 = 0.462 \text{ V}$$

$$\therefore Cu + 2Ag^{+} \rightarrow Cu^{2+} + 2Ag; \quad E^{\circ}_{cell} = 0.462 \text{ V}$$

Hence, the galvanic cell in question will consist of **anode of copper and cathode of silver.**

Calculation of concentration :

$$E^{o}_{cell} = \frac{0.059}{n} \log \frac{[\text{Products}]}{[\text{Reactants}]} \quad [\because E_{cell} = 0]$$

$$0.462 = \frac{0.059}{2} \log \frac{0.01}{[Ag^{+}]^2} \qquad [n=2]$$

$$\frac{462 \times 2}{59} = \log(10^{-2}) - \log[Ag^{+}]^2$$

$$\frac{924}{59} = -2 - 2\log[Ag^{+}] \ \Rightarrow [Ag^{+}] = \mathbf{1.48 \times 10^{-9}\ M}$$

58. $E^{o}_{cell} = \frac{0.0591}{n} \log K_c$ **or** $\frac{RT}{nF} \log K_c$

Let us split the desired reaction into two half cell reactions:

Oxidation half reaction :

$$H_2O + \frac{1}{2} H_2(g) \rightleftharpoons H_3O^{+} + e^{-} \qquad E^{\circ} = 0.00 \text{ V}$$

Reduction half reaction :

$$H_2O + e^{-} \longrightarrow \frac{1}{2} H_2 + OH^{-} \qquad E^{\circ} = -08.277 \text{ V}$$

Net reaction :

$$2H_2O \rightleftharpoons H_3O^{+} + OH^{-} \qquad E^{\circ}_{cell} = -0.8277 \text{ V}$$

So, the number of electrons involved in redox reaction, $(n) = 1$

We know that $E^{\circ}_{cell} = \frac{0.0591}{n} \log K_c$

$$\log K_c = \frac{E^{\circ}_{cell} \times n}{0.0591} = \frac{(-0.8277) \times 1}{0.0591} = -14.005$$

$K_c = \text{Antilog}[-14.005] = \mathbf{9.88 \times 10^{-15}}$

59. For a concentration cell

$$E_{cell} = \frac{0.059}{n} \log \frac{C_1}{C_2}$$

It is a concentration cell as both the electrodes are made of same element. Negative electrode acts as anode in a galvanic cell.

At anode; $H_2 \longrightarrow 2H^{+} + 2e^{-}$ $\qquad [H^{+}] = 10^{-6}$ M

At cathode; $2H^{+} + 2e^{-} \longrightarrow H_2$ $\qquad [H^{+}] = ?$

$$E_{cell} = \frac{0.059}{1} \log \left[\frac{C_{H^{+}}}{10^{-6}}\right] \text{ or } 0.118 = \frac{0.059}{1} \log \left(\frac{C_{H^{+}}}{10^{-6}}\right)$$

$$\log \frac{C_{H^{+}}}{10^{-6}} = \frac{0.118}{0.059} = 2 \Rightarrow C_{H^{+}} = \mathbf{10^{-4}\ M}$$

60. Half cell reactions will be

$$Zn^{2+} + 2e^{-} \rightleftharpoons Zn \quad \text{......}(i)$$

$$H^{+} + e^{-} \rightleftharpoons \frac{1}{2} H_2 \text{ or } 2H^{+} + 2e^{-} \rightleftharpoons H_2 \quad \text{......}(ii)$$

We know that $E_{Zn/Zn^{2+}} = E_{Zn/Zn^{2+}} - \frac{RT}{nF} \ln \frac{[Zn^{2+}]}{[Zn]}$

Here, $R = 8.314$ Jmol^{-1} K^{-1}, $T = 298$ K, $F = 96{,}500$ c/eq., $n = 2$, $E^{\circ}_{Zn/Zn^{2+}} = 0.76$ V.

Substituting the values in the above equation

$$E_{Zn/Zn^{2+}} = 0.76 - \frac{8.314 \times 298}{2 \times 96500} \ln \frac{0.1}{1} = 0.79 \text{ V}$$

$$\text{Similarly, } E_{H^{+}/H_2} = E^{\circ}_{H^{+}/H_2} - \frac{RT}{nF} \ln \frac{[H_2]}{[H^{+}]^2}$$

$$= 0 - \frac{8.314 \times 298}{2 \times 96500} \ln \frac{[1]}{[H^{+}]^2}$$

$$= 0.05915 \log_{10}[H^{+}] = -0.05915 \text{pH}$$

$$(\because -\log_{10}[H^{+}] = \text{pH})$$

Now since $E = E_{Zn/Zn^{2+}} + E_{H^{+}/H_2}$

$$0.28 = 0.79 - 0.05915 \text{ pH} \Rightarrow \text{pH} = \frac{0.51}{0.05915} = \mathbf{8.62}$$

61. (i) The two half cell reactions can be written as below :

Oxidation half reaction : $Zn \rightarrow Zn^{2+} + 2e^{-}$

Reduction half reaction : $Cu^{2+} + 2e^{-} \rightarrow Cu$

Thus the cell reaction will be : $Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$

(ii) EMF of cell, $E^{\circ}_{cell} = E^{\circ}_{cathode} - E^{\circ}_{anode}$

$$E^{\circ}_{cell} = 0.350 - (-0.763)$$
$$= 0.350 + 0.763 \text{ volts} = \mathbf{1.113\ volts}$$

(iii) Since emf of the cell is **positive**, the reaction as written is **spontaneous**.

62. (a)

$$\underset{\substack{2[119 + (2 \times 35.5)] \\ = 380}}{2SnCl_2} \longrightarrow \underset{119}{Sn} + \underset{\substack{119 + (4 \times 35.5) \\ = 261}}{SnCl_4}$$

$\because$ 119g Sn deposits from = 380g $SnCl_2$

$\therefore$ 0.119g Sn deposits from $= \frac{380}{119} \times 0.119 = 0.380\text{g } SnCl_2$

$\because$ 380g $SnCl_2$ gives = 261g $SnCl_4$

$\therefore$ 0.380 g $SnCl_2$ gives $= \frac{261}{380} \times 0.380 = 0.261\text{g } SnCl_4$

$\therefore$ Wt of $SnCl_2$ left after decomposition
$= 19.00 - 0.380 = 18.620$ g.

Ratio $SnCl_2 : SnCl_4$
$\Rightarrow$ 18.620 : 0.261 $\Rightarrow$ **71.34 : 1**

(b) $NaCl \xrightarrow{\text{Electricity}} Na^+ + Cl^-$

At Cathode; $Na^+ + e^- \longrightarrow Na$

$2Na + H_2O \longrightarrow 2NaOH + H_2$

At anode; $Cl^- \longrightarrow Cl + e^-$

$Cl + Cl \longrightarrow Cl_2$
$2OH^- + Cl_2 \longrightarrow Cl^- + OCl^- + H_2O$
$OCl^- + 2HOCl \longrightarrow ClO_3^- + 2Cl^- + 2H^+$

$Na^+ + ClO_3^- \longrightarrow \underset{\text{Sod.Chlorate}}{NaClO_3}$

On prolonged electrolysis
$ClO_3^- + ClO^- \longrightarrow Cl^- + ClO_4^-$
$Na^+ + ClO_4^- \longrightarrow \underset{\text{Sod. perchlorate}}{NaClO_4}$

(c) Charge on $N^{3-} = 3$
No. of ions in 14 g of $N^{3-} = 6.02 \times 10^{23}$

No. of ions in 1g of $N^{3-} = \frac{6.02 \times 10^{23}}{14}$

No. of electronic charges on 1 g $N^{3-} = \frac{6.02 \times 10^{23}}{14} \times 3$

Charge on 1 g of N^{3-}

$$= \frac{6.023 \times 10^{23} \times 3 \times 1.6 \times 10^{-19}}{14} \text{ Coulombs}$$

($\because$ Charge on one electron is 1.6×10^{-19} Coulombs)
= 2.06×10^4 Coulombs